Evaluation of Organic-Hydrofluoric Acid Mixtures for Sandstone Acidizing

BY

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DEDICATED TO MY FATHER'S SOUL, MY MOTHER, MY WIFE AND MY SON NADER

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Thesis Abstract

Full Name of Student: Bader Ghazi Suraihan Al-Harbi

Title of Study: EVALUATION OF ORGANIC-HYDROFLUORIC ACID MIXTURES FOR SANDSTONE ACIDIZING

Major Field: Petroleum Engineering

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Different organic-HF acid mixtures have been used to stimulate sandstone formations. Typically, they are used as alternative to regular mud acid in order to overcome its potential limitations such as rapid spending, high corrosion rate and incompatibility with sensitive clays.

This study focuses on identifying the type of precipitations that occur during reactions of organic-HF acids and on determining the factors that affect these precipitations. This work also provides a systematic investigation of the chemical interactions of various sandstone minerals with three different organic-HF acids over a wide range of parameters. Finally, the results of coreflood experiments using organic-HF acid mixtures are presented. In addition, this study highlights the main findings and recommendations as well.

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في هذه الرسالة تم تقييم عدة مخاليط من الاحماض العضوية وحمض الفلور لتحفيز الصخور الرملية. عادة, يتم استخدام الاحماض العضوية كبديل لحمض الكلور لتجنب السلبيات مثل التفاعل السريع, التآكل و عدم التوافق مع بعض انواع الصخور. تركز هذه الرسالة على التفاعلات بين هذه الاحماض وانواع مختلفة من الصخور والترسبات التي تتكون اثناء هذه التفاعلات والعوامل التي تؤثر عليها. كما يوفر هذا العمل تحقيق منهجي للتفاعلات الكيميائية بين الاحماض والصخور تحت عدة متغيرات. أخيرا, تعرض نتائج تجارب "الكورفلود". بالإضافة إلى ذلك, فإن هذه الدراسة تلقي الضوء على النتائج والتوصيات الرئيسية.

درجة ماجستير العلوم

جامعة الملك فهد للبترول والمعادن

الظهران-المملكة العربية السعودية

مايو 2012

CHAPTER 1

1.1 INTRODUCTION

Reservoir stimulation is considered to be one of the most important activities of the production engineer. It is a technique used to improve the gas and oil well deliverability and injectivity as well. There are several stimulation techniques, implemented to achieve the stated purpose, such as acid wash, matrix acidizing, acid fracturing and propped fracturing.

Acid wash is mainly used to dissolve acid soluble scales in the well bore, Figure1and perforations by pumping an acid at the desired position excluding reservoir formation (Williams et al. 1979).There are various types of scale and these scales can cause significant reduction in well productivity.A normalized distribution of scale samples collected from different sour gas producers is shown in figure 2 (Franco et al 2010). The scale was composed mainly of iron sulfide, iron oxide hydroxide and iron carbonate. Additionally, calcium carbonate and barium sulfate are also present in some samples. In acid wash treatments, it is recommended to circulate the acid (HCl or organic acid) in order to accelerate the dissolution process by increasing the transfer rate of unspent acid to the wellbore surface and also to avoid formation damage caused by the reaction products precipitate from the spent acid (William et al 1979).

Figure 1: Scale deposit on pipe wall.

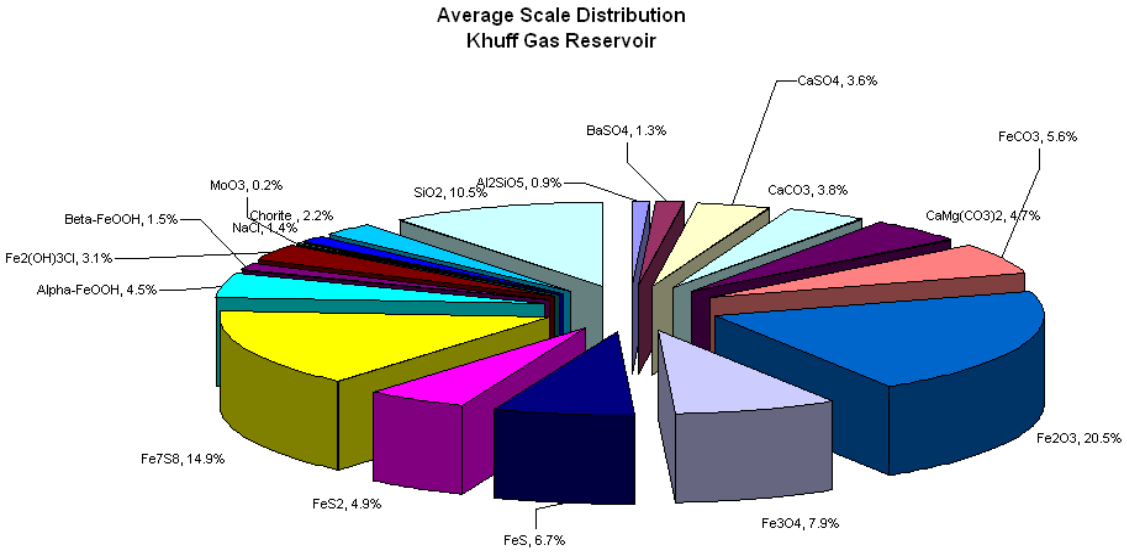

Figure 2: Normalized distribution of mineral scales found in several samples collected from the tubular of different gas producers (Franco et al 2010).

Matrix acidizing is a technique used to clean the near wellbore area in order to increase productivity or injectivity by injecting acid below fracture pressure. It is intended to recover the permeability in the near wellbore (i.e. critical area) by dissolving some formation minerals and foreign materials such as drilling mud (McLeod 1984). The matrix acid treatment is effective especially in damaged well with a near wellbore flow restrictions (Gatewood et al 1970 and McCune et al 1975). In carbonate formations, HCl based acids, organic acids and chelating agents are employed while HF based acids including mud acid, organic mud acid, chelating agent-HF are used to stimulate sandstone formations.

Acid fracturing is the injection of fluid into the formation at a pressure high enough to fracture the formation or open existing fractures (William et al 1979). Stimulation is achieved when a highly conductive flow channel remains open after fracturing, Figures 3 and 4. Acid fracturing is the most widely used acid treatment for limestone and dolomite formations. Similar to other well stimulation techniques, acid fracturing is intended to reduce the skin effect. Various HCl based systems are used to create deep etches fractures. However, there are some limitations associated with the use of HCl such as rapid reaction rate and high corrosion rate. Because of the fast reaction rate of HCl with limestone and dolomite, the conductivity of created fracture is low. Hence, several acid systems have been developed to tackle these challenges. These include gelled acid, in-situ gelled acid, emulsified acid, visoelastic surfactant based acids and organic acids.

Propped fracturing is the injection of fluids carrying proppant at pressure greater than fracture pressure. After the closure, the proppant remains in the fracture providing high conductive channels. Hydraulic fracture is beneficial in low to moderate permeability reservoirs where the near wellbore damage removal is not sufficient to obtain an attractive productivity.

Conventional fracturing fluids include water based and polymer containing fluids, hydrocarbon based fluids, energized fluids and foams. Unconventional fracturing fluids, on the other hand, include non-polymer containing fluids such as viscoelastic surfactant fluids, methanol containing fluids, liquid CO_2 based fluids and liquefied petroleum gas based fluids (Gupta 2009).

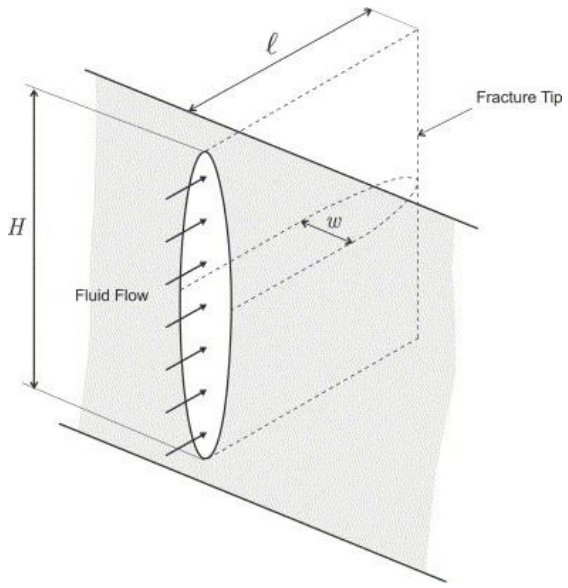

Figure 3: Typical Fracture.

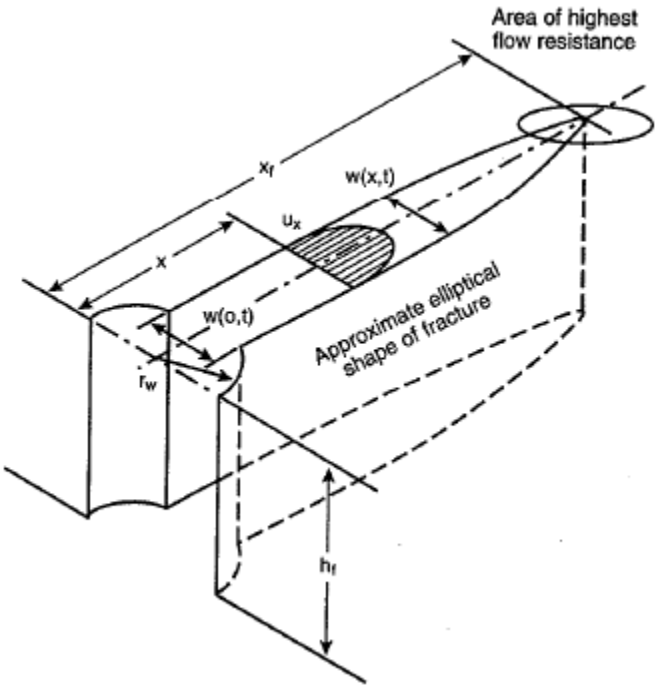

Figure 4: Typical Fracture.

1.2 MATRIX ACIDIZING

If k_s is less than k, then s is positive indicating formation damage. Vice versa, negative skin factor denotes stimulation. **Figures 5 and 6** show the near wellbore area with an altered permeability. Significant reduction in flowing bottom hole pressure occurs due to positive skin factor resulted from formation damage, **Figure 7**. In real situation, higher pressure drop is required to achieve similar production to ideal one.

For undamaged well,

$$q = \frac{kh(P_s - P_{wf,ideal})}{141.2B\mu * \ln\left(\frac{r_s}{r_w}\right)} \quad (1)$$

For damaged well,

$$q = \frac{k_s h(P_s - P_{wf,real})}{141.2B\mu * \ln\left(\frac{r_s}{r_w}\right)} \quad (2)$$

Where P_s: pressure at boundary of damaged zone

$P_{wf,ideal,}$, $P_{wf,\ real}$: Flowing bottom hole pressure in undamaged and damaged well respectively

r_e: reservoir radius

r_w: wellbore radius

r_s: radius of damaged zone

$$\frac{J_s}{J_o} = \frac{F_k \log\left(\frac{r_e}{r_w}\right)}{\log\left(\frac{r_s}{r_w}\right) + F_k \log\left(\frac{r_e}{r_w}\right)} \quad (3)$$

Where F_k: k_s/k_o the permeability ratio

J_o: the undamaged formation productivity

J_s: damaged formation productivity

The production changed due to damage or stimulation can be determined from **Figure 8** which shows the ratio of damage over undamaged productivity versus depth of damaged zone. At certain damaged over undamaged permeability, there is a decrease in productivity ratio as the depth of damage increases. Additionally, the decrease in productivity ratio is drastic at lower permeability ratio i.e. more damage. Similarly, the improvement in well productivity after acid treatment can be estimated using Figure 8. For example, if the damage zone extends 10 inches with permeability ratio equal to 0.2, the productivity is equivalent to 0.6 of undamaged well. If the damaged is removed completely, the production rate will increase 1.6 folds. In comparison, if the depth of damaged zone and permeability ratio are 10 inches and 0.1 respectively, there will be a 2.5 fold increase in production rate. Hence, matrix stimulation is more effective in damaged well. Figure 9 also shows the increase productivity ratio after acid treatment as a function of depth of acid contact.

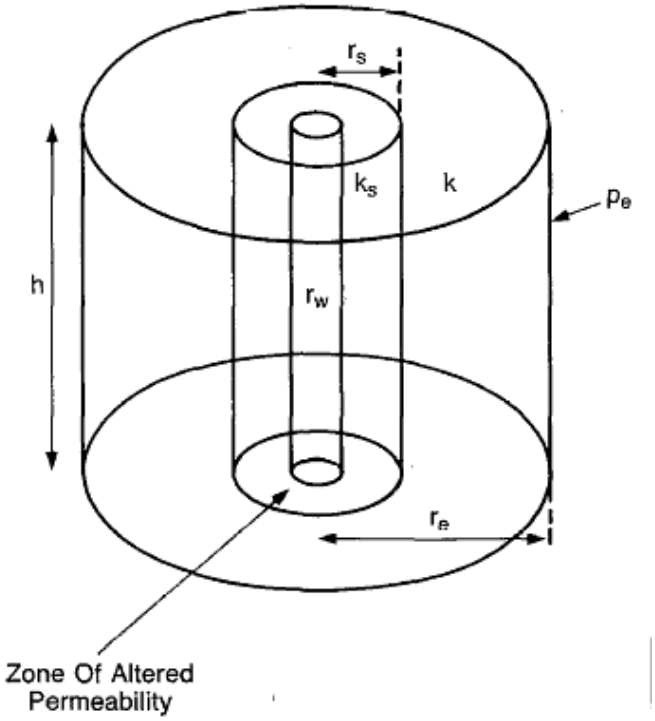

Figure 5: Near wellbore zone with altered permeability (Bert et al. 1979).

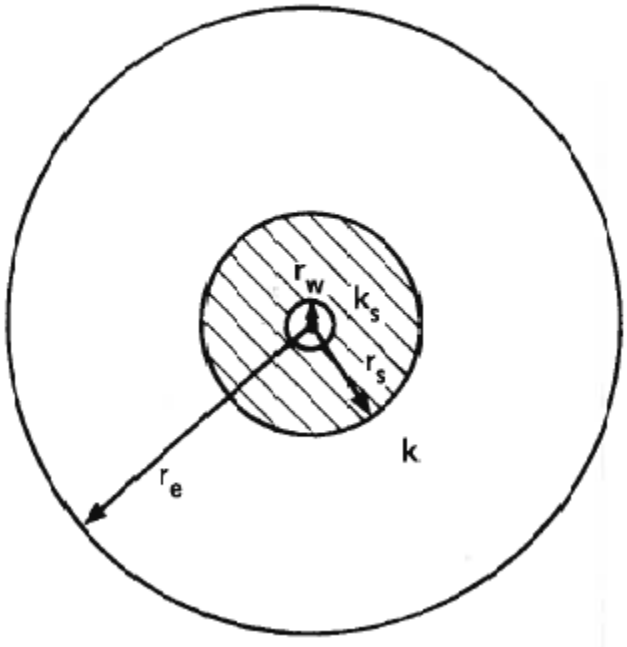

Figure 6: Schematic of a damaged well (Bert et al. 1979).

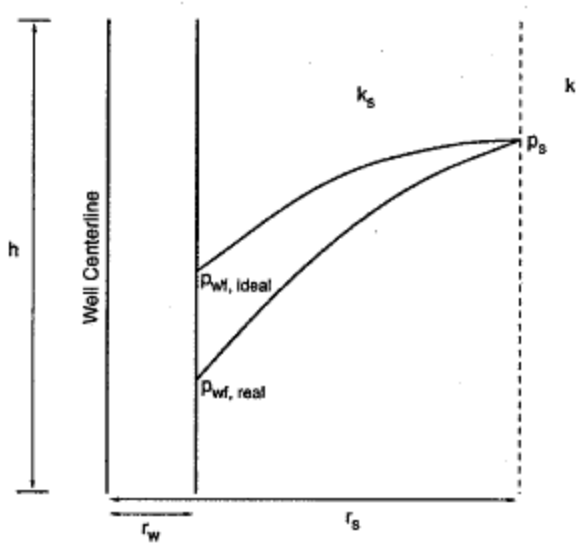

Figure 7: Ideal and real flowing bottom hole pressure vs distance from near wellbore (Bert et al. 1979).

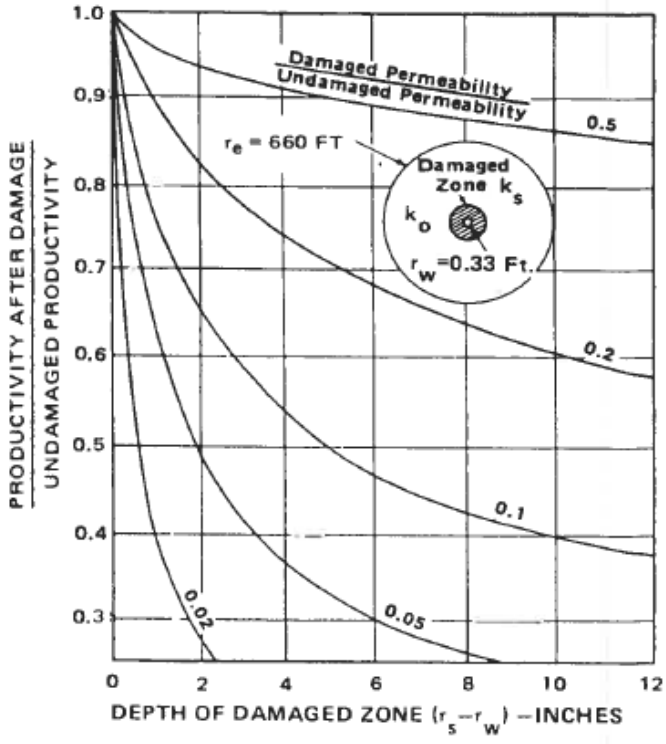

Figure 8: Production loss due to formation damage (Bert et al. 1979).

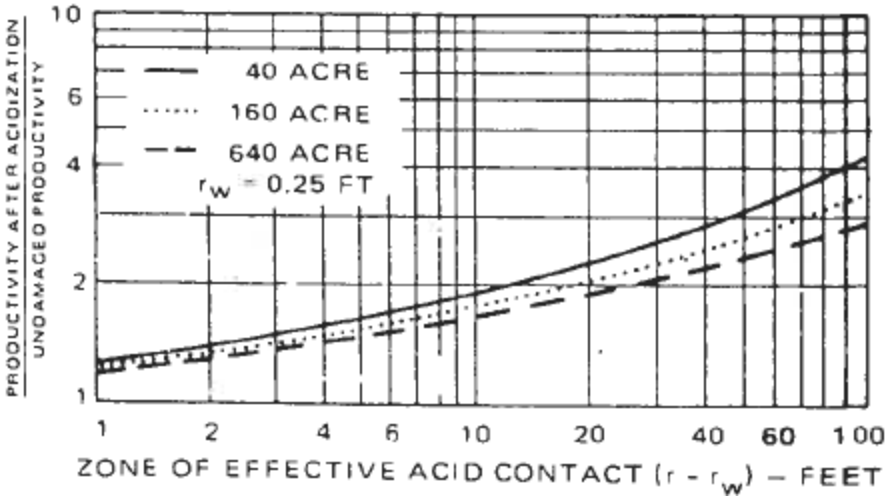

Figure 9: productivity ratio after acid treatment (Bert et al**.** 1979).

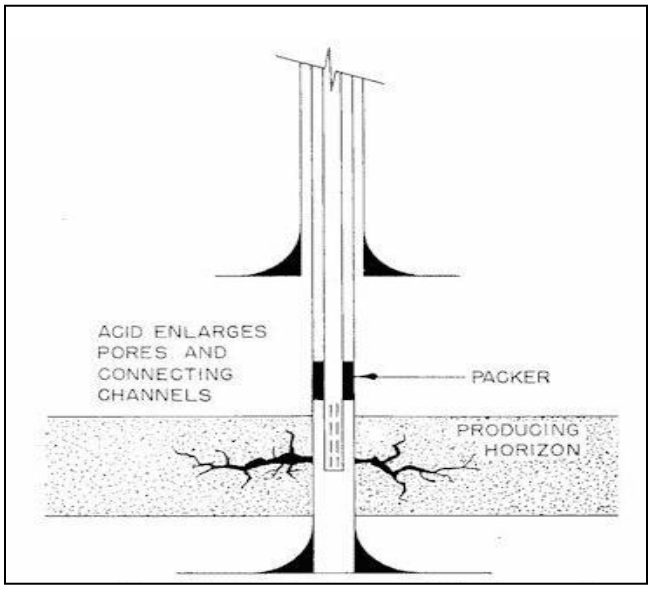

Figure 10: Wormhole created after matrix acidizing.

1.3 STATEMENT OF PROBLEM

Different organic-hydrofluoric acid mixtures have been used to stimulate sandstone formations. They are used to tackle some challenges associated with the use of regular mud acid such as rapid spending, high corrosion rate and incompatibility of HCl with some sensitive clays.

Although field applications have shown that organic-HF mixtures can be effective sandstone stimulation fluids, however, there is a lack in deep understanding of these systems. Investigating the interaction of organic-HF acids with sandstone minerals and identifying the potential damaging precipitation will help in optimizing their applications.

1.4 RESEARCH OBJECTIVES

This work, for the first time, provides a systematic investigation of the chemical interaction between various sandstone minerals (namely, silica, kaolinite, Illite and chlorite) and three different organic-HF acids over a wide range of parameters. Hence, the comparison is made at the same conditions of temperature, acid/rock ratio and reaction time. In addition, chelating tests will be performed to identify the type of precipitate and determine the critical pH where precipitation starts to form as well as to assess the chelating power of each acid used in this study. Finally, coreflood experiments will be conducted to evaluate organic-HF acids.

1.5 RESEARCH METHODOLOGY

1.5.1 Chelating Test

1. All instruments used in these tests must be not made of glass to avoid the reaction between glass and HF.
2. 6 acid mixtures including (9%Formic&1%HF, 10%Acetic&1%HF, 10%Citric&1%HF, 9%Formic&1.5%HF, 10%Acetic&1.5%HF and 10%Citric&1.5%HF) will be prepared.
3. The tested acid will be poured in separate plastic tubes.
4. Certain amount of aluminum chloride salt is added into the acid to have 1000mg/L Al, 5000mg/L and 10,000 mg/L Al.
5. The mixture containing 10,000 mg/L Al is shaked well and then pH is measured using Orion pH meter.
6. The mixture is neutralized by adding NaOH.
7. The pH is measured and the liquid will be analyzed using ICP.
8. As soon as the precipitation occurs, the pH is recorded as the pH of precipitation.
9. At the end of this test, the solid sample will be analyzed to know the type of precipitation.

1.5.2 Solubility Test

The main objective of this set of experiments is to study the reactivity of each individual clay with organic-HF systems under wide range of parameters. By analyzing the liquid and solid samples, it would be possible to know which acid is more susceptible to precipitation and which one is capable of leaching more aluminum and silicon i.e. more reactive.

1. Silica and 3 different clays namely kaolinite, chlorite and illite are analyzed by XRD to determine the actual percentage of the desired compound.

2. Around 8g of the tested acid is added to 2 g of the individual solid either silica or clay.
3. The mixture is kept at 50^{o}C for 1hr.
4. After one hour, the sample is filtered and then the liquid is analyzed by ICP for aluminum and silicon while the solid sample is analyzed by either XRD or XRF.
5. The test is repeated but with extended time namely 2 hr and 4 hr
6. The test is also repeated at 75^{o}C.

1.5.3 Coreflood Test

The coreflood experiments are used to simulate the reservoir conditions. Based on the results obtained from the previous tests, the optimum acid concentrations will be used to acidize the core plugs.

1. Plug, 1.5 inches in diameter and 3 inches in length, is fixed in a core holder.
2. A pump is used to pressurize the core holder with pressure equals to the overburden pressure in the selected well.
3. The temperature of the oven is set to be equivalent to the reservoir temperature.
4. ammonium chloride solution is pumped through the core to calculate the permeability of the core based on Darcy law.
5. A preflush with organic acid is pumped to remove the calcite from the core.
6. The main acid having organic-HF, ammonium chloride, is injected through the core for stimulation by removing mainly the clays.
7. Overflush containing ammonium chloride is pumped to calculate the permeability after the stimulation.
8. The two calculated permeability values are compared to evaluate the effectiveness of the acid system used for stimulation.

CHAPTER 2

LITERATURE REVIEW

In any acid treatment, there are two reactants namely formation rocks and injected acids. The fluid selection is highly dependent on the formation mineralogy and the type of damage.So, in the following sections, types of formations and acids that are widely used for each formation are described.

2.1 FORMATION MINERALOGY

Petroleum reservoir is a permeable and porous underground formation containing hydrocarbon (oil and/or gas) migrated from a source rock. The hydrocarbon is trapped in a sedimentary rock and cannot move out of it because of the geometry of the layer or its properties, the properties of adjacent layers. The most reservoir rocks are limestones, dolomites, sandstones or a combination of these.

Carbonate is a sedimentary rock and classified mainly as limestones and dolomites. It makes up 20 to 25 percent of all sedimentary rocks. Limestone is composed primarily of calcite ($CaCO_3$) while in dolomite calcium is partially replaced by magnesium to form calcium magnesium carbonate ($CaMg(CO_3)_2$). So, the carbonate rock is predominately composed of calcium, magnesium and carbonate. Element oxides include CaO, MgO and CO_2 constitute more than 90 percent of the average carbonate rock.Additionally, siderite is a principal mineral in carbonate rocks altered by Fe-bearing solutions **(Sam Boggs 2006).**

Sandstone makes up 20 to 25 percent of sedimentary rocks **(Sam Boggs 2006).** Sandstone formation is predominantly composed of silica and it is cemented by clays, feldspar and/or carbonate. Silica has a stable structure and small specific area compared to clays and feldspars. Kaolinite is a tetrahedral sheet of Si linked to an alumina octahedral sheet of oxygen, **Figure 11 (Walsh *et al*. 1982, Mitchell 1993)**. Illite is composed of an aluminum sheet, which is sandwiched by two silica layers, **Figure 12**. Some randomness in the stacking of layers in illite might occur. Chlorites are 2:1:1 phyllosilicates minerals. They have a structure that have layer of octahedrally-coordinated Si, Al and Fe in the interlayer space. The 2:1 layers are formed by the stacking of two sheets of tetrahedrally-coordinated silica, and one sheet of octahedraly coordinated Fe or Al between the two tetrahedral sheets, **Figure 13 (Walsh *et al*. 1982, Mitchell 1993)**.

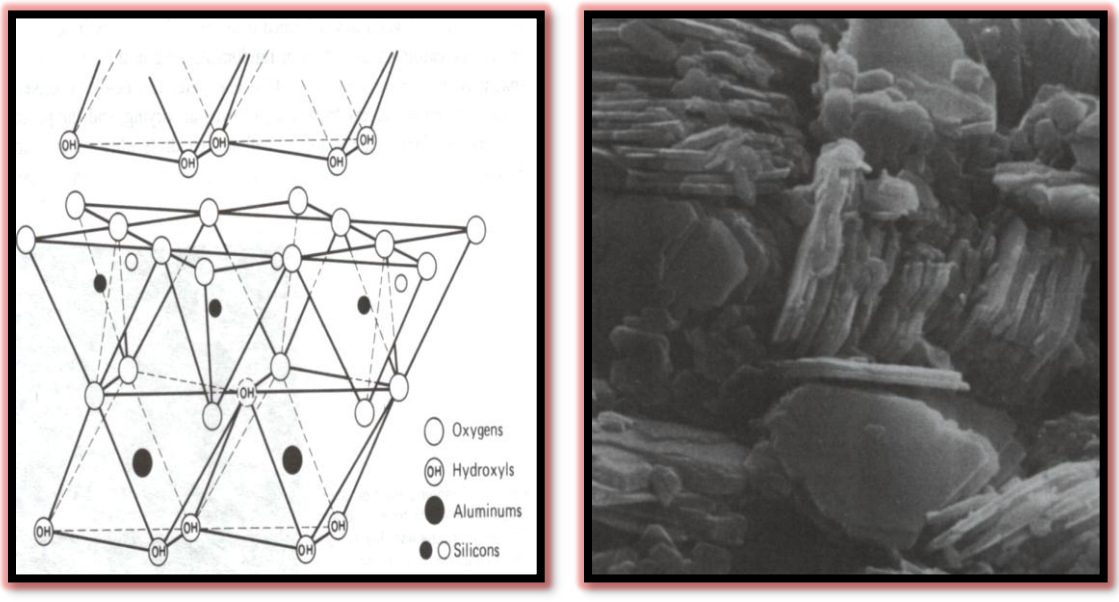

Figure 11: Crystalline structure of Kaolinite (Walsh *et al*. 1982).

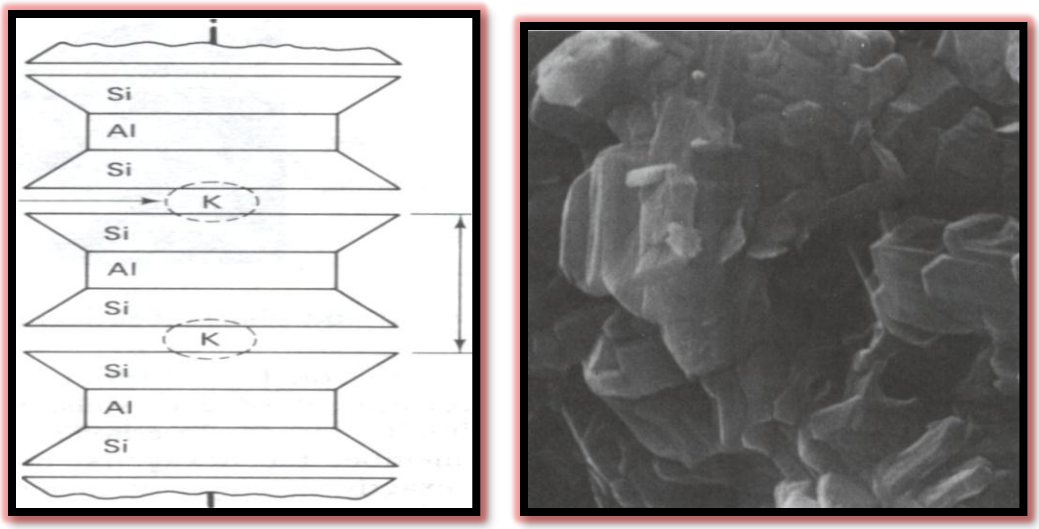

Figure 12: Crystalline structure of illite (Walsh *et al*. 1982).

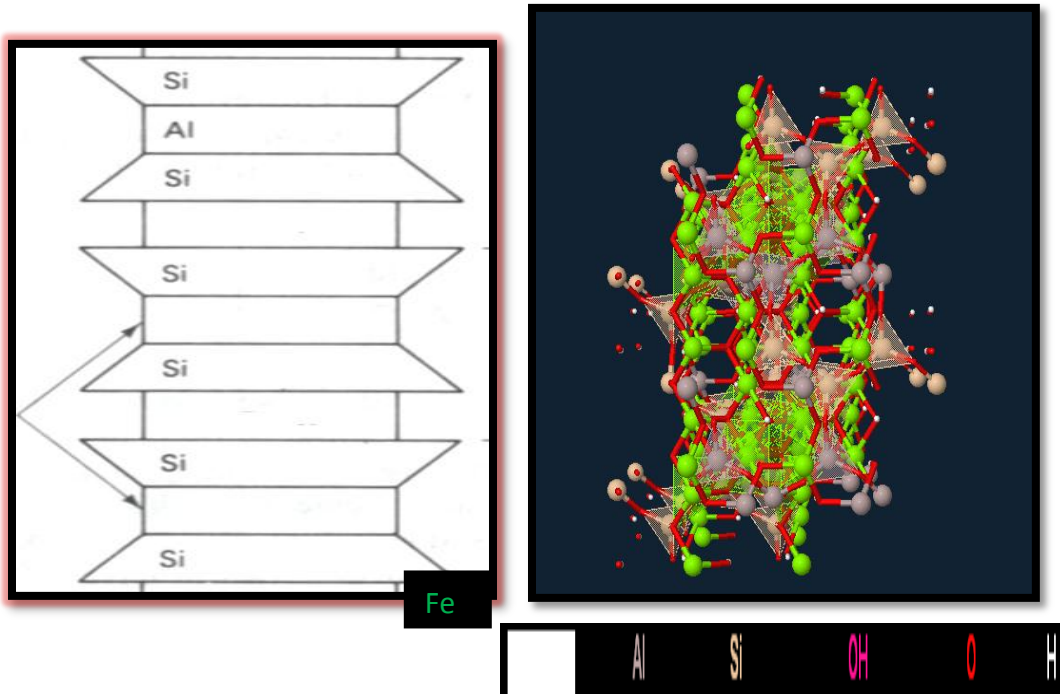

Figure 13: Crystalline structure of chlorite (Walsh *et al*. 1982).

2.2 CARBONATE ACIDIZING

The most common acid used in carbonate acidizing is hydrochloric acid and this is mainly attributed to its low cost and high dissolving power. However, rapid spending and high corrosion rates were the main concern during carbonate acidizing using HCl. Hence, several approaches have been tried to retard the reaction rate of HCl with the rock including the use of emulsified acid (Navarrete et al 1998), gelled acid (Nasr-El-Din et al 2008),visco-elastic surfactants(David et al 2003 and Al-Mohammad et al 2006) and organic acids (Harris 1961 and Chang et al 2008). The reactions between HCl with calcite and dolomite are simple, Eqs 4 and 5.

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O \quad (4)$$

$$CaMg(CO_3)_2 + 4HCl \rightarrow CaCl_2 + MgCl_2 + 2CO_2 + 2H_2O \quad (5)$$

2.2.1 Emulsified Acids

Emulsified acids consist of hydrochloric acid as internal phase and diesel or xylene as external phase. Emulsified acid can provide deeper penetration because of its retarded nature as diesel acts as a diffusion barrier between the acid and the rock. Besides, due to its relatively high viscosity, emulsified acid has better sweep efficiency and thus improve acid distribution in heterogeneous reservoirs (Buijse 2000). Another advantage of emulsified acid is the lower corrosion rate because it has minimum contact of the tubular.

2.2.2 Gelled Acids

In gelled acids, the early stages are used to block the treated zones and force the next acid stages to the unreacted zones. Retardation in this acid results from the reduction in the rate of acid transfer because of high viscosity.

2.2.3 Organic Acids

Due to their low corrosivity and retarded nature, organic acids were preferred over many other acid mixtures. Acetic acid and formic acids are typically used at concentrations less than 13wt% and 9wt% respectively. This is because at these concentrations, reaction products like organic salts of calcium and magnesium are soluble in spent acid (Robert and Crowe 2000). Additionally, citric acid and lactic acid are employed in stimulating carbonate formations. Organic acids do not react to their full acid capacity in presence of their reaction products.

$$CaCO_3 + 2HA \rightleftharpoons CaA_2 + H_2O + CO_2 \qquad (6)$$

2.3 SANDSTONE ACIDIZING

A typical sandstone acid treatment involves preflush, main flush and post-flush.

Preflush

Preflush containing mainly HCl or organic acids is injected prior to the main flush in order to displace the hydrocarbon and formation brine away from the wellbore and thus prevent the formation of sodium and potassium fluorosilicate. Additionally, preflush is intended to dissolve carbonate to minimize calcium fluoride precipitation.

Main Flush

Several acid systems based on hydrofluoric acid have been developed over the years. The main aim was to design such effective system to achieve the following objectives; to retard acid rock interaction as means to achieve deeper penetration, to have less aggressive acid and to avoid undesirable reactions and subsequently prevent formation damage (Rae and Di-Lullo 2003). While HF is the main reactant, HCl is inevitably added into the mixture to maintain acidic environment and subsequently prevent precipitations of HF reaction by-products. The presence of strong acid is also necessary to reduce the HF consumption.

Mud acids containing different HCl/HF ratios have been extensively used to dissolve primarly clays, feldspars and to less extent silica and thus increase well productivity or injectivity**(Smith and Hendrickson 1965, Gidley 1985, Brady *et al.* 1989, Shuchart 1995, Gdanski and Shuchart 1996, Thomas *et al.* 2001, Hartman *et al*. 2003, Taq*et al*. 2009)**. Despite the reasonable success of mud acid, critical drawbacks associated with using the mud acid have limited its use. One of the most potential limitations of mud acid is rapid spending, especially at elevated temperatures, which results in subsequent precipitations of reaction products following secondary and tertiary reactions and limits acid penetration in the formation as well **(Gdanski 1996, Thomas *et al.* 2001)**. A combination of these precipitations, matrix unconsolidation, presence of HCl-sensitive clays, and high corrosion rates has resulted in variable success rate of mud acid stimulation treatments or even worse in further formation damage **(Simon and Anderson 1990, Gdanski 1996, Thomas *et al.* 2002)**.

Several attempts have been made in order to tackle these potential problems encountered with acidizing using strong mud acids. These include adjusting HCl/HF ratios and use of retarded mud acids **(Gdanski 1985, Gdanski 1996, Gdanski and Shuchart 1996, Al-Dahlan *et al.***

2001). As HCl/HF ratio increases, low F/Al ratios are found and thus fluoride becomes more efficient in dissolving alumino-silicates **(Shuchart 1995).** However, these methods remained prone to the same mud acid problems at elevated temperature values. Several research studies have revealed that retarded mud acids provided only marginal reduction in mud acid reaction rate with aluminosilicates and their reactions created new precipitation types. For example, fluoboric-based retarded mud acid will form potassium-based precipitate, KBF_4, when it reacts with either illite or K-feldspars and aluminum chloride HF retarded system is very susceptible to aluminum fluoride precipitation **(Al-Dahlan *et al.* 2001)**. Another approach to improve the effectiveness of sandstone acidizing involved the use of organic-HF acids **(Walter and Keeney 1978, Abrams *et al*. 1983, Stoessell and Pittman 1990, Motta *et al*. 1996, Shuchart and Gdanski 1996, Shuchart 1996, Gdanski and Shuchart 1997)**.

Due to their retarded nature and low corrosion rates, organic-HF acids provided an excellent alternative to regular mud acid mixtures, especially in high temperature formations **(Gdanski and Shuchart 1997)**. Additionally, the use of organic-HF acids has become imperative in formations containing HCl-sensitive clays such as illite**(Abrams *et al*. 1983)**. The two main used organic-HF acids are based on acetic and formic acids. Besides acetic and formic-HF, citric mud acid has been also used **(Robert and Crowe 2000)**. All these acids rely on the same reaction retardation mechanism, which is the slow release of HF acid through their reaction with ammonium bi-fluoride salt (ABF), NH_4HF_2.

Retarded HF Acids

This is a summary of the main retarded HF systems. Retarded HF acid based on Fluoboric acid (HBF_4). Fluoboric acid slowly hydrolyzes in aqueous solution to generate HF according to Eq. 7. So, as HF reacts and spends on the formation rocks, more HF is generated. Another

advantage of this system is the ability to stabilize clays and thus prevent fines migration and clay swelling.

$HBF_4 + H_2O \longrightarrow HBF_3OH + HF$ (7)

Retarded HF acid based on $AlCl_3$. Aluminum fluoride complexes are generated as aluminum chloride reacts with HF (Eq. 8).

$AlCl_3 + 4HF + H_2O \longrightarrow AlF_4^- + 3HCl + H_3O^+$ (8)

Upon the reaction and spending of HF on formation rocks, AlF^-_4 hydrolyzes to generate HF (Eq. 9)

$AlF_4^- + 3H_3O^+ \longrightarrow AlF^{+2} + 3HF + 3H_2O$ (9)

Retarded HF based on phosphonic acid. This acid is composed of phosphonate compounds including phosphonate acids and salts and esters combined with HF. HF can be introduced to the system by hydrolyzing ammonium bifluoride.

Organic HF Acid Mixtures

Edwin A. Richardson 1975

In this invention, a way of maintaining a relatively slow rate of reaction is provided by limiting the concentration of hydrogen fluoride and ionized weak acid in the solutions. These concentrations are kept low by the buffering action of the mixtures of weak acids and weak acid salts that are dissolved in the solutions.

Templeton et al 1975

This paper describes laboratory work on the use of methyl formate to generate formic acid and then generating HF by reacting with ammonium fluoride as shown in Eqs. 10 and 11.

$HCOOC_3 + H_2O \rightarrow HCOOH + CH_3OH$ (10)

$HCOOH + NH_4F \rightarrow NH_4^+ + HCOO^- + HF$ (11)

Two batches of clay have been used in this study. In these runs, HF dissolved clay under low acidity conditions (pH>4). However, there was a precipitation equivalent to one third the dissolved clay. XRD analysis of the filtered residue showed that 60% bentonite and 40% ralstonite ($(Na_2Mg)F_2.3Al(F,OH)_3$) clearly indicating fluoride based precipitation. ralstonite has high solubility in 7.5 % HCl. Moreover, such solid in case not completely removed would be re-deposited deeper in the formation and thus minimum formation damage would be expected.

Also, field tests have shown that an NH_4F-$HCOOCH_3$ solution can effectively treat oil wells and the increase in production lasted longer period of time compared to conventional mud acid treatments.

Motta et al 1996

First, cement solubility tests were performed to compare different acid formulations in terms of the cement degradation. 10%Acetic/1.5%HF had 0% solubility while 6% HCl/1.5%HF dissolved 13% by weight. Coreflood apparatus was utilized with the following injection stages: CO_2 to remove air from the plug, 3% ammonium chloride to measure initial permeability, HCl or acetic acid to remove carbonate, HCl/HF or acetic/HF to compare the responses and finally 3% ammonium chloride to measure final permeability. Five core flood tests with 10%acetic/1.5%HF and five with 10%acetic/1%HF were performed. There was neither damage nor improvement in the permeability of these clean plug samples. Motta also reported two successful field trials. 10%Acetic acid/1%HF was used in both trials and the injectivity increased 22 and 40 times in the first and second treatments respectively.

Shuchart et al 1996

The author reported two field treatments using acetic-HF and formic-HF. In both treatments, there was a significant precipitation of aluminum fluoride particularly in acetic-HF system. To

study the interaction of organic-HF systems with the formation minerals and the potential precipitation, batch reactions with only kaolinite at 75^{o}F and 200^{o}F were conducted. The following acids were evaluated in this set of experiments: 10%formic-1%HF, 10%formic-1.5%HF, 10%acetic-1%HF, 10%acetic-1.5%HF and two new systems based on organic acid. Also, column packed tests (90% sand& 10% bentonite) were performed to compare the performance of 10%acetic-1%HF with new system based on organic acid. The permeability increased from 20 mD to 25 mD when the column was treated with acetic-HF. In the other system, the overall permeability increased from 20 mD to 35 mD. While formic-HF treatment failed to give sustained production increases, the new system treatment in the same well resulted in three fold production increase that lasted for more than 4 months.

Baofeng et al 2000

Based on the results of solubility tests conducted on reservoir samples, a new low-damage acetic-HF acid system dissolved almost 35 % of the rock which is comparable to what has been dissolved by 10%HCl-1%HF. Core flood tests were also performed on sandstone rocks. There was a significant reduction in the permeability when 12%HCl-3%HF was used whereas there was 350% increase in permeability when the new system was used. The results of field treatment indicated the capability of this new system to increase the injectivity of one treated water injection well from 0 to 100 m^3/D and lasting for more than half a year.

Wehunt et al 1993

In this paper, several acids were tested using flow test including three organic acids namely acetic, propanoic and butanoic acid. Among these acids, acetic-HF acid was the most effective one. Beside, 10%acetic-0.05%HF and 10%acetic-0.1%HF worked better than systems with higher HF concentrations i.e. 10%acetic-1.5%HF.

2.4 ORGANIC-HF ACIDS CHEMISTRY

The common method to prepare mud acid is by dissolving ammonium bifluoride (ABF) salt in hydrochloric acid (HCl), as shown in **Eqs. 12** and **13**:

$$HCl \rightarrow H^+ + Cl^- \qquad (12)$$

$$H^+ + NH_4HF_2 \rightarrow NH_4Cl + 2HF \qquad (13)$$

According to **Eq. 13**, HF acid will be generated by reaction of hydronium ion with ABF. Since HCl is a strong acid, the generation rate of HF acid from ABF will be high. Unlike HCl, organic acids are weak and their dissociation reactions, release of hydrogen ion, are slow. Consequently, in organic-HF mixtures, the formation of HF acid is retarded due to low concentration of H^+ ions. In other words, the generation of hydrofluoric acid, in organic-HF mixtures, is controlled by slow equilibrium dissociation reactions of weak organic acids. Upon the reaction of HF acid with formation minerals, the equilibrium of organic mud acid is upset, which triggers the activation of new HF formation cycle by more weak acid ionization.

Acetic and formic acids are mono-protic acids, while citric is a tri-protic acid and dissociates step-wise. **Eqs. 14-18** show dissociation reactions of acetic, formic and citric acids, respectively **(Martell and Smith 1976, Perrin 1981, Al-Khaldi *et al*. 2005)**:

$$CH_3COOH \leftrightarrow CH_3COO^- + H^+, \qquad pK_a = 4.756 \qquad (14)$$

$$HCOOH \leftrightarrow HCOO^- + H^+, \qquad pK_a = 3.75 \qquad (15)$$

$$H_3C_6H_4O_6OH \leftrightarrow H_2C_6H_4O_6OH^- + H^+, \qquad pK_{a1} = 3.128 \qquad (16)$$

$$H_2C_6H_4O_6OH^- \leftrightarrow HC_6H_4O_6OH^{2-} + H^+, \qquad pK_{a2} = 4.76 \qquad (17)$$

$$HC_6H_4O_6OH^{2-} \leftrightarrow C_6H_4O_6OH^{3-} + H^+, \qquad pK_{a3} = 6.4 \qquad (18)$$

The dissociation degree of each acid is measured by its pK_a value. Acids with low pK_a values are stronger than the ones with higher pK_a. In comparison, citric acid is the strongest acid, highest dissociation degree, followed by formic and then acetic acid. The pK_a values also determine the distribution of ionic species. **Figures 14-16** show the distribution of the ionic species of acetic, formic and citric acids, respectively, as a function of solution pH. The conjugate bases of acetic, formic and citric acids have the ability to chelate different ions such as aluminum and iron, present in organic-HF and aluminosilicates reaction solutions **(Serjeant and Dempsey 1979, Hall and Dill 1988, Rietjens 1998)**.

The affinity of conjugate base (ligand), A^{n-}, for different ions, M^{m+}, is dependent on stability of the formed conjugate base and ion complex molecule. The chelation ability, affinity, is defined by the formation constant, K_F, **Eqs. 19**and **20**:

$$A^{n-} + M^{m+} \leftrightarrow MA^{m-n} \qquad (19)$$

$$K_F = \frac{[MA^{m-n}]}{[M^{m+}][A^{n-}]} \qquad (20)$$

The larger the formation constant, the stronger is the ion-conjugate base complex. **Table 1** lists the acetic, formic and citric acid complexes with aluminum and iron (III). This chelation ability of different organic acids is one of the main factors which govern the precipitation of aluminum fluoride, as will be discussed later.

Table 1: Organic acids-metals stability constants (Martell and Smith 1976).

	Log K_F at 25 °C		
Ligand	Al^{3+}	Fe^{3+}	Ca^{2+}
Acetate (CH_3COO^-)	1.51	3.4	1.18
Formate ($HCOO^-$)	1.36	3.1	1.43
Citrate ($C_6H_4O_6OH^{3-}$)	11.7	11.5	3.5

Similar to organic acids, HF is a weak acid and it does not completely dissociate, **Eq. 21 (Perrin 1981)**:

$$HF \rightarrow H^+ + F^-, pK_a = 3.170 \qquad (21)$$

Figure 17 shows that the amount of both HF and free fluoride ions is dependent on solution pH value. For example, at pH value of 2, the amount of free F^- ions is only 5%, and it increases to almost 85% when pH value reaches 4. The interaction of free F^- ions with dissolved ions, from HF reaction with sandstone minerals, can result in formation of precipitates. Thus, the presence of free F^- will have a major impact on the organic-HF acids reactions with aluminum silicates, as will be discussed later.

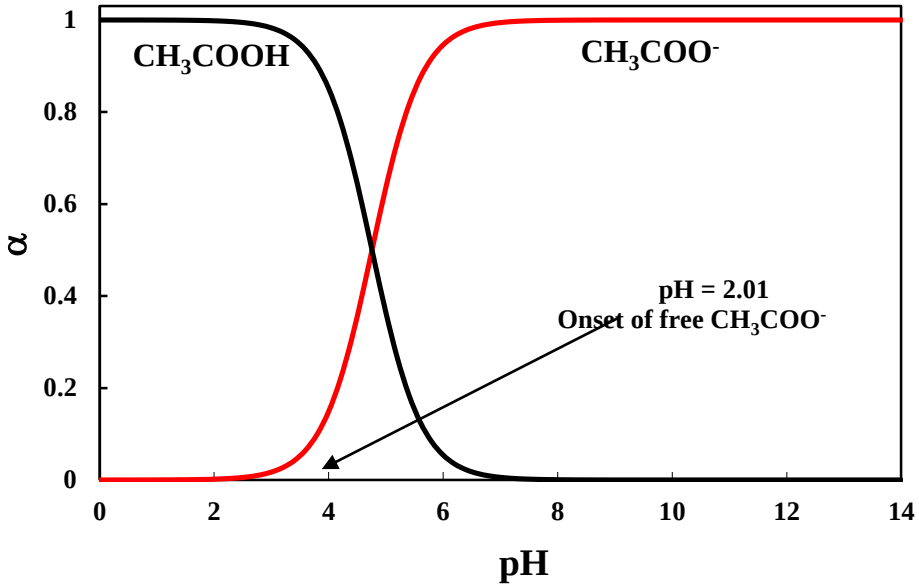

Figure 14: Distribution of acetic acid species as a function of solution pH value, using Eq. 14.

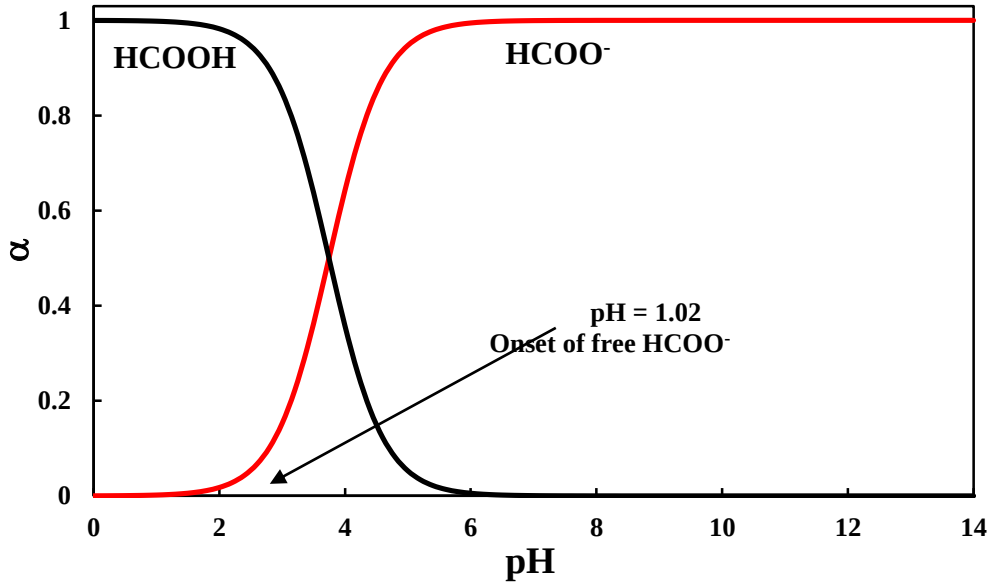

Figure 15: Distribution of formic acid species as a function of solution pH value, using Eq. 15.

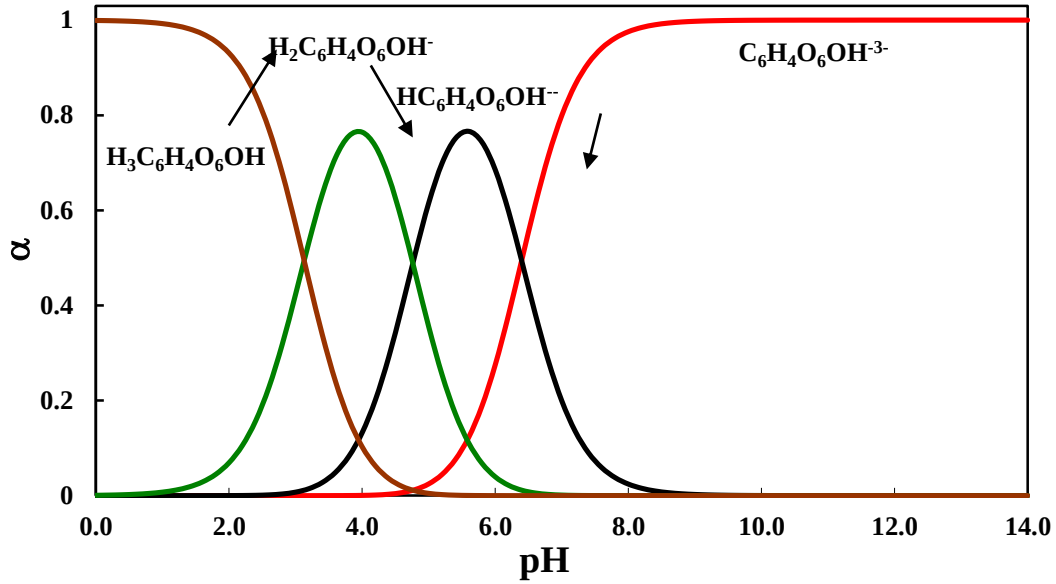

Figure 16: Distribution of citric acid species as a function of solution pH value, using Eqs. 16-18.

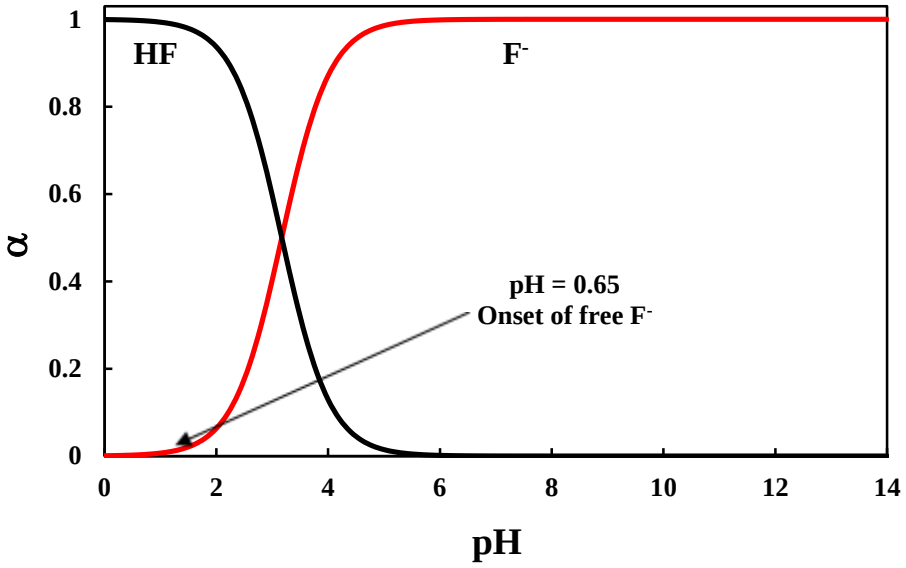

Figure 17: Distribution of hydrofluoric acid species as a function of solution pH value, using Eq. 21.

2.5 REACTION OF HF WITH QUARTZ AND ALUMINOSILICATE

The reaction of HF acid with sandstone minerals involves several and complex interactions. This is mainly due to mineralogy diversity of sandstone formations. The predominant mineral in sandstone formations is quartz and it is cemented by clays, alkaline aluminosilicate and/or carbonate (calcite, dolomite, and ankerite). Hydrofluoric acid preferentially reacts with clays, feldspars and to less extent with quartz.

Silica (SiO_2) has a stable structure and small specific surface area compared to aluminosilicates as shown in **Table 2**. Consequently, its reaction rate with hydrofluoric acid is slower when compared with that of clays and feldspars. The silica reacts with HF to produce silica tetra-fluoride (SiF_4) which, in turn, reacts with HF to yield fluosilicic acid (H_2SiF_6) as a final product, **Eqs. 22**and **23 (Yokel 2002)**:

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O \qquad (22)$$

$$SiF_4 + 2HF \rightarrow H_2SiF_6 \qquad (23)$$

Table 2: Specific surface area of sand, feldspar and clay minerals (Al-Dahlan 2001)

Mineral	Specific surface are, m^2/g
Quartz (SiO_2)	2
k-feldspar ($KAlSi_3O_8$)	5-29
Illite/smectite $KAl_4(Si_8,Al)O_{20}(OH)_4/(Ca,Na)(Al,Mg,Fe)_4(Si,Al)_8O_{20}(OH)_4$	82
Kaolinite ($Al_2Si_2O_5(OH)_4$)	15.5
Illite	100-150
Chlorite ($Fe_5Al)(AlSi_3)O_{10}(OH)_8$	20-40
Bentonite	80-700

Fluosilicic acid is also produced by HF reaction with clay minerals (aluminosilicates), **Eq. 24 (Yokel 2002)**:

$$Al_2Si_2O_5(OH)_4 + 18HF \rightarrow 2H_2SiF_6 + 2Al^{3+} + 6F^- + 9H_2O \quad (24)$$

The reactivity of different clays with HF varies due to the huge difference in their structure **(Perrin 1981)** and specific surface area **(Gidley 1985)**. For example, kaolinite ($Al_2Si_2O_5(OH)_4$) has a tetrahedral sheet of silica linked to an alumina octahedral sheet through oxygen, while illite has a three layer crystalline structure where the octahedral alumina sheet is at the center between two tetrahedral silica sheets.

Although all reaction products of HF primary reaction with sandstone minerals, shown in **Eqs. 17-19**, are soluble; however, they might undergo secondary or tertiary reactions and produce insoluble products. Upon consumption of HF, fluosilicic acid decomposes to HF and silicon tetra-fluoride, which then undergoes hydrolysis to form silica gelatious precipitate**, Eqs. 25** and **26 (Shaughnessy 1981)**:

$$H_2SiF_6 \rightarrow 2HF + SiF_4 \quad (25)$$

$$SiF_4 + 4H_2O \rightarrow Si(OH)_4 + 4HF \quad (26)$$

Besides insoluble secondary reaction products, silica gel, aluminum fluoride is another insoluble product which could be produced from tertiary reactions, **Eq. 27 (Crowe 1986)**:

$$3F^- + Al^{3+} \rightarrow AlF_3 \quad (27)$$

During the secondary reaction, the sodium and potassium concentrations increase continuously according to Eq. 28 to a point where they will react with unreacted fluosilicate and precipitates as sodium or potassium fluosilicate (Gdanski).

$$H_2SiF_6 + 6MAlSi_3O_8 + 18\ HCl \quad 6M^+ + 6AlF^{2+} + Cl^- + 18H_2SiO_3 + SiO_2 2H_2O \quad (28)$$

This secondary reaction is probably a fast reaction so there will be a concern due to precipitating these compounds near well bore causing more severe damage (Bryant).

The formation of these precipitates in spent organic-HF reaction solutions will be discussed in detail.

Calcium Fluoride

Calcium fluoride precipitates due to the primary reaction

$$CaCO_3 + 2HF \leftrightarrow CaF_2\downarrow + H_2O + CO_2 \qquad (29)$$

The main sources of calcium are calcium carbonate in the rock and lost circulation materials, and formation water. To avoid this type of formation damage, a preflush with hydrochloric acid or organic acid is used to dissolve calcium and thus prevent the contact of calcium and HF acid.

Iron Hydroxide

There are many sources of iron including surface and subsurface equipment and some formation minerals like chlorite, smectite and siderite as presented in **Eq. 30-32**.

$$(5+x)\ HF + M\text{-}Al\text{-}Si + (3-x+1)\ H^+ \longrightarrow HSiF_5 + AlF_x^{(3-x)+} + M^+ + H_2O \qquad (30)$$

$$x/5\ HSiF_5 + M\text{-}Al\text{-}Si + (3-x+1)\ H^+ + H_2O \longrightarrow AlF_x^{(3-x)+} + M^+ + \text{silica gel} \qquad (31)$$

$$AlF_x + M\text{-}Al\text{-}Si + H^+ \longrightarrow AlF_y + M^+ + SiO_2xH_2O \qquad (32)$$

However, the state of iron differs according to the source. For example, the majority of iron dissolved in solution during acid treatments is present in Fe (II) state while more Fe (III) is found in oxygen corrosion products. Similarly, most of the iron contained in formation minerals is Fe (II). Thus, the type of precipitate and conditions of precipitate formation will differ accordingly. Ferric (III) and ferrous (II) hydroxide precipitate in spent acid when pH rises to around 1 and 6, respectively, according to the following two equations **(Taylor *et al.* 1999)**:

$Fe^{3+} + 3OH^- \leftrightarrow Fe(OH)_3.mH_2O$ pH above 1 (33)

$Fe^{2+} + 2OH^- \leftrightarrow Fe(OH)_2.nH_2O$ pH above 6 (34)

According to above equations, only Fe $(OH)_3$ is considered to be a potential precipitate in almost all pickling and acid treatments resulting in formation damage in the critical area. However, in the presence of fluoride ions, there are two schools of thoughts with regards to iron based precipitation. Shaughnessy *et al.* (1981) reported that iron hydroxide precipitation is not formed in presence of fluoride ions due to high affinity of iron toward fluoride. In contrast, Crowe (1985) stated that aluminum fluoride complexes are stronger than iron fluoride and thus the iron based precipitation will not be prevented by fluoride ions.

Iron Sulphide

A potential damaging compound in sour gas wells is iron sulphide. The existing iron containing sulphides are re-dissolved by acid and under certain conditions re-precipitate as iron sulphide. This precipitation mechanism can be illustrated by equations 35 through 39. Sulphide is highly reducing agent and thus almost no ferric ions exist in solution. In this case, ferric hydroxide no longer exists while iron sulphide is a problematic which starts precipitating at pH around 1.9.

$Fe + H_2S \rightarrow FeS + H_2$ (35)

$FeS + 4HCl \rightarrow FeCl_2 + H_2S + 2HCl$ (36)

$H_2S \rightarrow H^+ + HS^-$ (37)

$HS^- \rightarrow H^+ + S^{2-}$ (38)

$FeCl_2 + S^{2-} \rightarrow FeS + 2Cl^-$ (39)

CHAPTER 3

RESULTS AND DISCUSSION (CHELATING TESTS)

In first set of experiments, aluminum chloride salt was added to organic-HF acids to have 1,000-10,000 mg/L of Al. **Figure 18** shows citric:HF (10/0.5 wt%) acid solutions containing various aluminum concentrations. There was no precipitation in any of these solutions. As described above, aluminum fluoride will not precipitate unless solution pH value exceeds 3.9 at 25^{o}C. The ability of citric:HF solutions to prevent aluminum fluoride precipitation was initially attributed to solution low pH value. Additionally, similar results were obtained when aluminum chloride salt was mixed with formic:HF (10/0.5 wt%), **Figure 19**. However, in acetic:HF (10/0.5 wt%) solutions white precipitate formed when Al level reached 1,000 ppm. At higher aluminum concentrations, > 1,000 mg/L, no precipitation was formed, **Figure 20**. In comparison, acetic acid is weaker than both formic and citric acid and as a result, its dissociation degree is less than that of both formic and citric acid. Therefore, acetic acid solutions will have high initial pH values compared to both formic and citric acid solutions, which explains why precipitation occurred in acetic acid solutions only, while no precipitate was formed when Al was added to formic and citric acid: HF solutions. The absence of white precipitate in acetic acid solutions containing high aluminum concentration, > 1,000 ppm, was found to be due to F/Al below critical value as will be discussed later. The white precipitate was identified using XRD and it was found to be aluminum fluoride AlF_3.

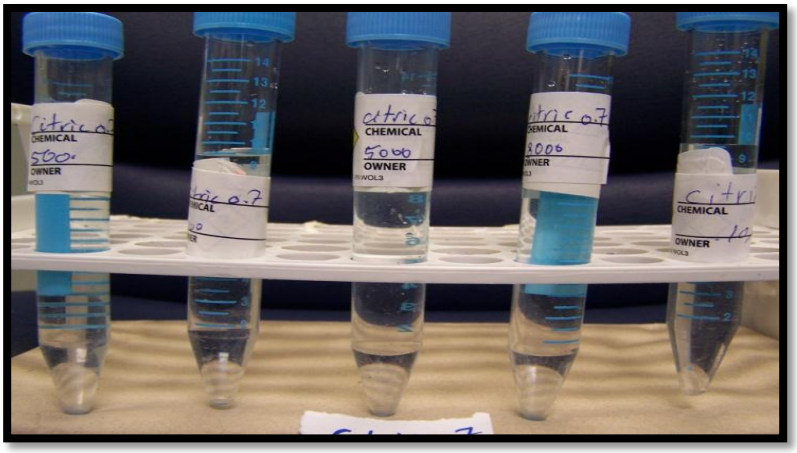

Figure 18: Citric:HF (10/0.5 wt%) containing 500; 1,000; 5,000; 8,000 and 10,000 mg/L Al from left to right.

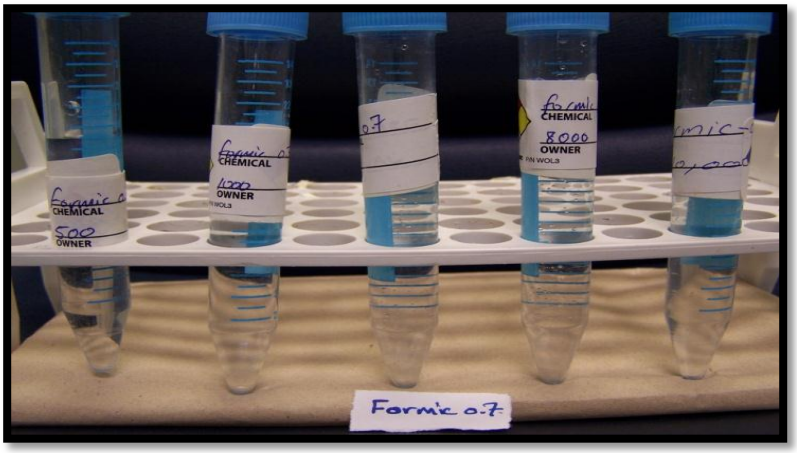

Figure 19 : Formic:HF (10/0.5 wt%) containing 500; 1,000; 5,000; 8,000 and 10,000 mg/L Al from left to right.

WHITE PRECIPITATE

AlF_3

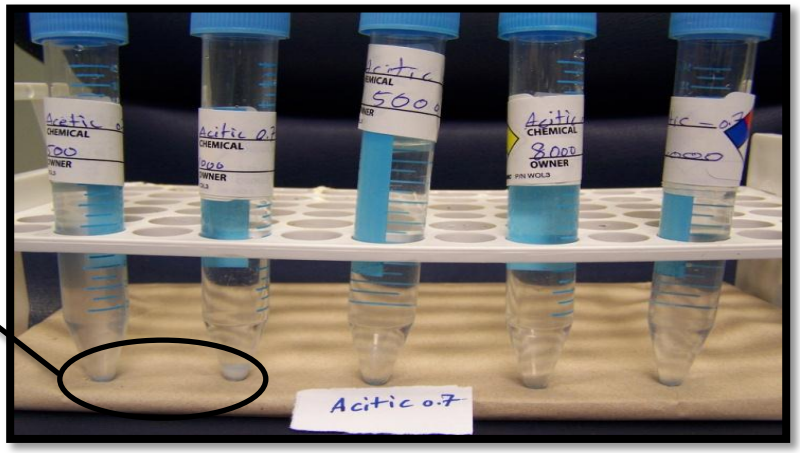

Figure 20: Acetic:HF (10/0.5 wt%) containing 500; 1,000; 5,000; 8,000 and 10,000 mg/L Al from left to right.

To further evaluate the ability of organic acids to prevent aluminum based precipitation, more fluoride was introduced into organic acid solutions. Different organic:HF solutions were prepared such that they contained 1.5 wt% HF. Aluminum chloride was added to formic, acetic and citric:HF (10/1.5 wt%) such that Al level varied between 1,000-10,000 ppm. In contrast previous results, the white precipitate (AlF_3), at this time, was formed in all organic:1.5wt% HF acids containing 1,000-8,000 mg/L of aluminum (**Figures 21-23**), while no precipitation occurred in all organic:HF solutions containing 10,000 ppm Al. Two main interesting trends were noticed from these results. First, when the HF concentration was raised from 0.5 to 1.5 wt%, aluminum fluoride precipitation occurred in all organic acids. This was mainly attributed to the fact that organic acids were consumed more in 1.5 wt% HF solutions to generate HF, **Eq. 20**. As a result, these solutions had higher pH value compared to 0.5 wt% HF solutions, which explains the formation of AlF_3 in 1.5 wt% HF solutions. However, another interesting trend is the absence of white precipitation in 1.5 wt% HF solutions containing 10,000 ppm Al, although they have high pH value. This indicated that there was another factor that governed the AlF_3 precipitation. **Table 3** summarizes the added and precipitated aluminum ions amounts in different organic:HF solutions. In general, the percentage of precipitation increased as more aluminum chloride is added to all solutions followed by a decrease at higher aluminum concentration. The precipitate completely disappeared when aluminum concentration was equal to 10,000 mg/L. This interesting trend was not dependent on pH value; instead, it was found to be dependent on Al/F ratio.

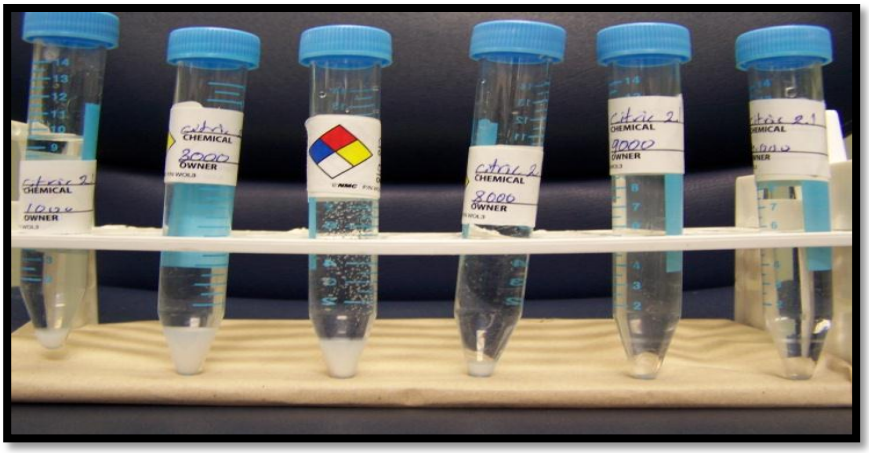

Figure 21: Citric:HF(10/1.5wt%) containing 1,000; 3,000; 5,000, 8,000; 9,000 and 10,000 mg/L Al from left to right.

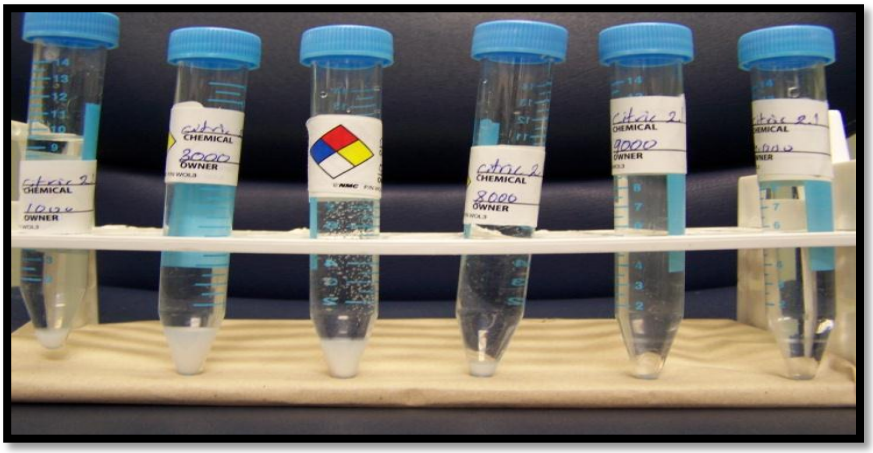

Figure 22: Formic: HF (10/1.5 wt%) containing 1,000; 3,000; 5,000, 8,000; 9,000 and 10,000 mg/L Al from left to right.

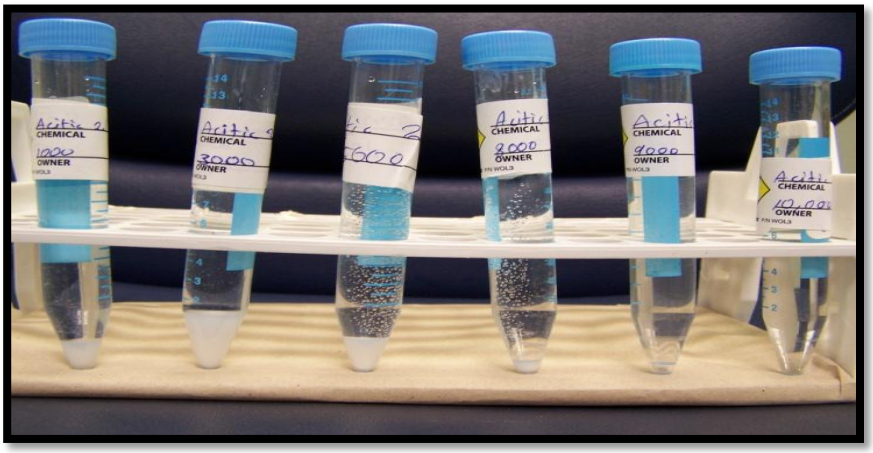

Figure 23: Acetic:HF (10/1.5 wt%) containing 1,000; 3,000; 5,000, 8,000; 9,000 and 10,000 mg/L Al from left to right.

Figure 24 shows the amount of dissolved aluminum concentration in all organic:HF (10/1.5 wt%) solutions as a function of F/Al ratio. It was noticed that dissolved aluminum was less than added aluminum amount, due to precipitation, only when F/Al ratio exceeded 1.9. At F/Al ratios below 1.9, no precipitation occurred and the dissolved aluminum concentration in all organic:HF (10/1.5 wt%) solutions was equal to the added amount of aluminum. At F/Al values above 1.9, the predominant aluminum fluoride complex seems to be AlF_3, which has very low solubility and precipitate once it forms.

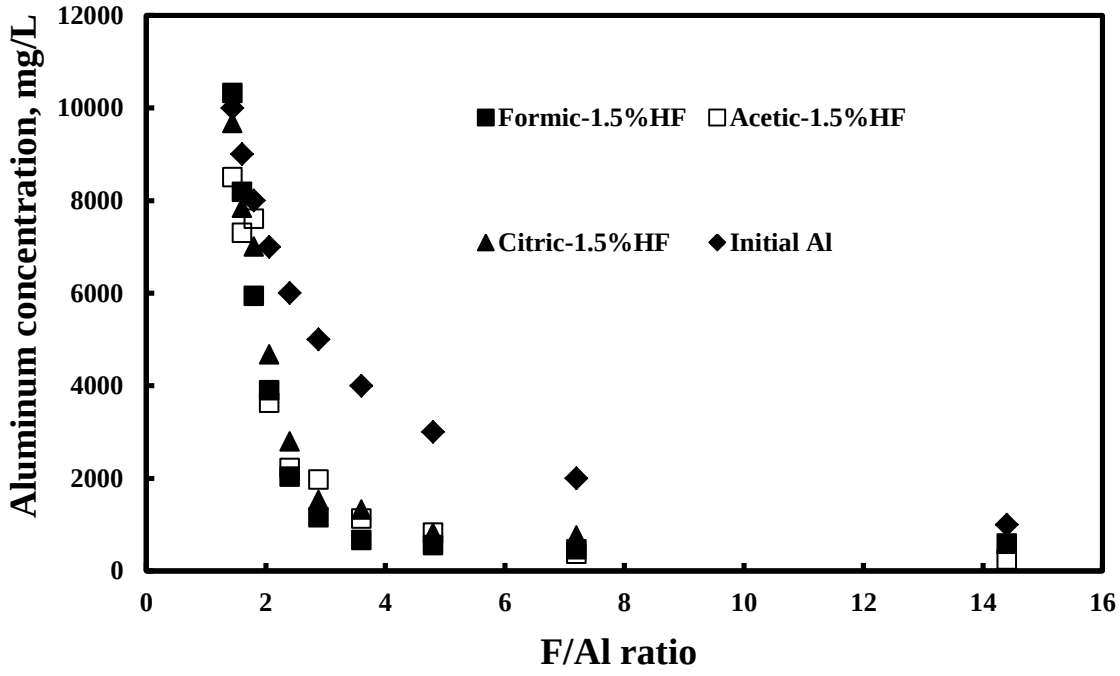

Figure 24: Aluminum concentration vs. F/Al ratio in Citric, Formic and Acetic acid containing 1.5 wt %HF.

To confirm the above conclusion, the previous set of experiments was repeated with organic acids containing 1.0 wt% HF. Similarly, aluminum chloride was added to these solutions such

that aluminum concentration varied between 1,000-10,000 ppm. Similar trend was observed with these solutions. Initially, aluminum fluoride precipitation occurred when aluminum chloride was first added. Then, at further addition of aluminum chloride, no precipitation occurred. The precipitation stopped in all solutions when added aluminum concentration reached 6,000 mg/L or above. This level of aluminum and fluoride corresponds to F/Al ratio of nearly 1.9. This confirms that, besides solution pH value, the aluminum fluoride precipitation is also dependent on F/Al ratio. This fact highlights the most important finding of this study. There are two factors play a significant role in the aluminum fluoride precipitation, namely: F/Ali ratio and pH value. Based on this finding, it is expected that aluminum fluoride precipitation is inevitable in organic:HF acids, especially that contain low aluminum concentration during early stages of acid treatment and this explained the severe aluminum fluoride precipitation suffered in acid treatments (**Schucart *et al.* 1996**). In comparison, organic:HF acids containing less HF concentration will suffer less aluminum fluoride precipitation due to the fact that the F/Al ratio will always less than that of organic:HF solutions containing relatively high HF level.

It is known that formate, acetate and citrate ions have affinity for aluminum. As a result, it was expected that the chelating power of organic acids will control aluminum-based precipitations. However, AlF_3 has high stability compared to organic acid conjugates with Al, **Table 1**, and apparently none of organic acids was able to prevent AlF_3 precipitation. However, the higher acidity of formic and citric acid contributed to have relatively less AlF_3 complex compared to acetic-HF acid, as was discussed earlier. One another explanation to the inability of organic acids to prevent AlF_3 could be the absence of conjugate bases at low pH values. This possibility was explored in detail.

Another set of experiments have been conducted to evaluate the ability of organic acid (acetic, formic and citric) to hold aluminum at high pH values. Organic:HF containing 10,000 mg/L of Al was neutralized by adding NaOH**. Figures 25, 26** and **27** show the aluminum concentration as a function of pH in formic:HF, acetic:HF and citric:HF, respectively. Both formic:HF and acetic:HF at (10/1.0 wt%) and (10/1.5 wt%) started to precipitate aluminum at pH around 5. The complete precipitation was observed at pH around 9 in both formic:HF and acetic:HF. Although these fluids initially were able to hold all dissolved aluminum ions at low pH value due to the fact that F/Al ratio is below 1.9. However, complete aluminum precipitation occurred at higher pH values. XRD analysis of the formed white precipitate showed that it was mainly $AlF(OH)_2$ which is different than that formed initially at high F/Al ratios. In contrast to formic and acetic:HF solutions, all added aluminum in citric:HF solutions remained in solution and no $AlF(OH)_2$ precipitation occurred at all range of pH values. The trend of aluminum precipitation in organic: 1.0 wt% HF was similar to that observed in organic:1.5wt% HF.

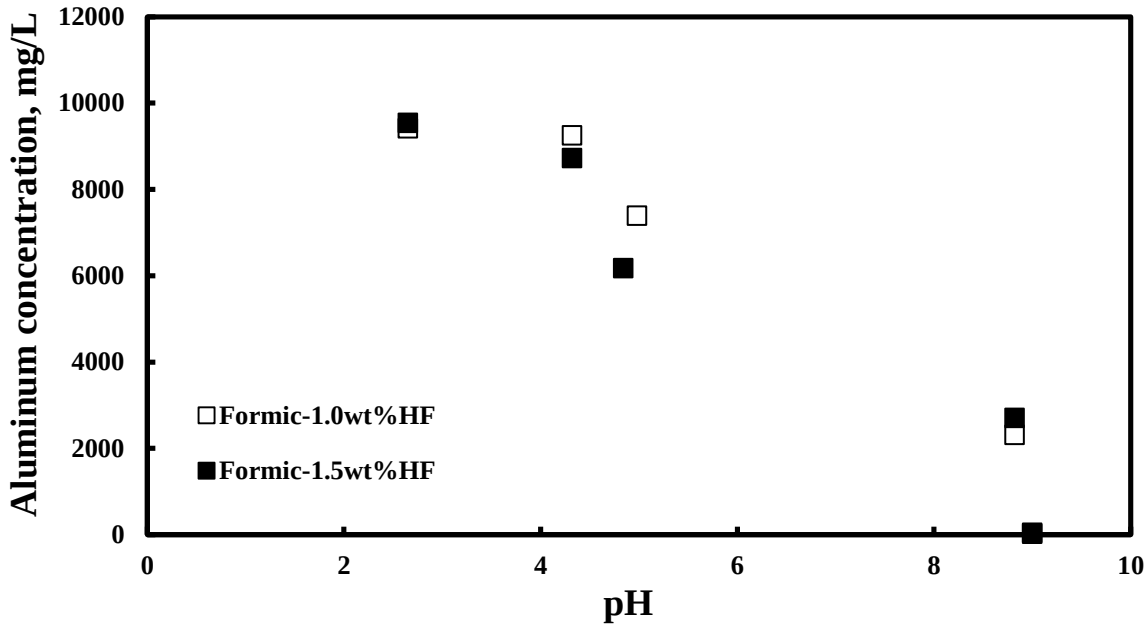

Figure 25: Aluminum concentration vs. pH in formic-HF acid containing initially 10,000 mg/L Al.

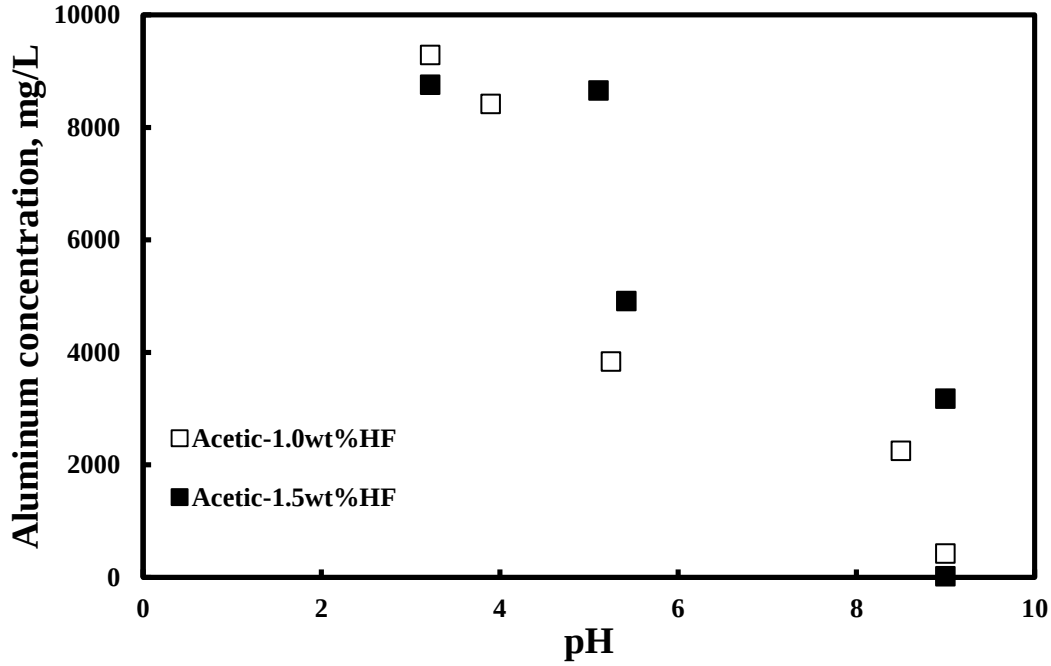

Figure 26: Aluminum concentration vs. pH in acetic-HF acid containing initially 10,000 mg/L Al.

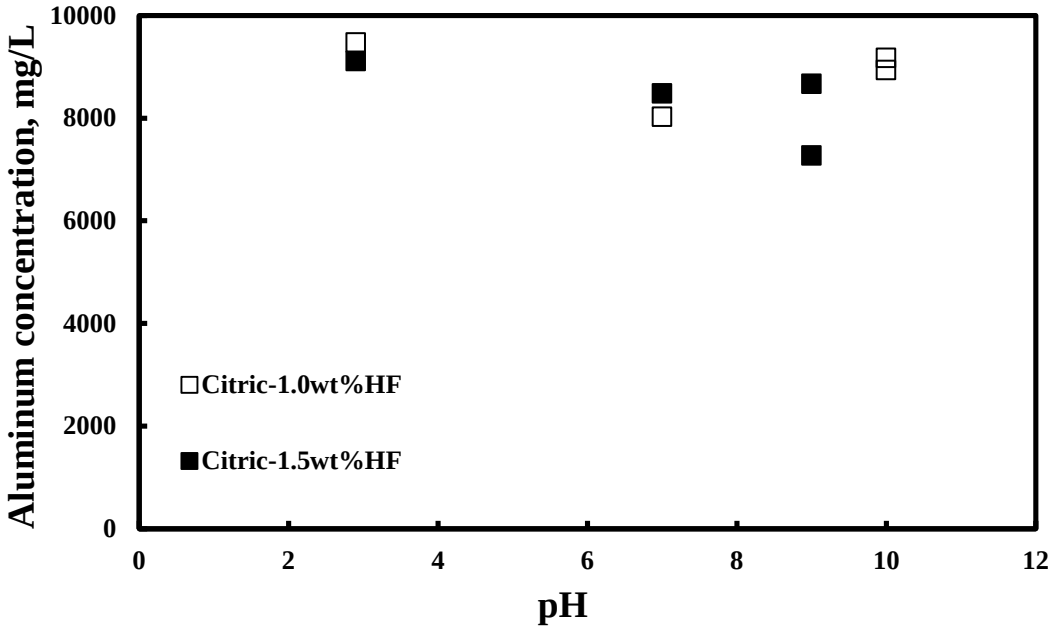

Figure 27: Aluminum concentration vs. pH in citric-HF acid containing initially 10,000 mg/L Al.

Similarly, iron chloride salt was mixed with separate organic:HF acid recipes to have 1,000; 5,000 and 10,000 mg/L Fe (III). Unlike organic-HF-aluminum mixtures, there was no indication of precipitation in all acid-iron mixtures in spite of high affinity of iron to fluoride especially at high fluoride iron ratios, **Table 3**. However, organic-HF acids were less effective at high pH values in terms of preventing iron based precipitation. As listed in **Table 4**, the amount of iron remained in solution decreased continuously in both formic:1.5wt% HF and acetic:1.5 wt% HF as pH increased. Similarly, in citric:1.5wt%HF there was iron precipitation in the beginning followed by increase in the iron concentration. This trend is similar to what noted when citric acid and iron mixtures were neutralized (**Taylor *et al.* 1999**). Organic:HF containing 5,000 mg/L of Fe had the same performance but complete precipitation occurred at pH range of 4 and 5. Additionally, at higher pH, citric:HF could hold more iron. On the other hand, complete precipitation was noted in organic:HF containing 1,000 mg/L Fe at comparable pH but none of these acids were able to re-dissolve the precipitate. The precipitate was identified to be Na_3FeF_6 and this is identical to the precipitate that was found in diluted mud acid (**Nasr-El-Din *et al.* 2002).** However, in mud acid two distinct precipitates were found i.e. Na_3FeF_6 and Na_4FeO_3 while in organic-HF acids only Na_3FeF_6 was identified.

Table 3: Added, detected aluminum concentration and % of precipitation in all organic: HF (10/1.5 wt%) acids.

Al concentration (mg/L)				**% precipitation**		
Added Al in solution	**Al in Formic:HF**	**Al in Acetic:HF**	**Al in Citric:HF**	**Formic:HF**	**Acetic:HF**	**Citric:HF**
1,000	593	248	583	40.7	75.2	41.7
2,000	467	369	763	76.7	81.6	61.9
3,000	557	824	818	81.4	72.5	72.7
4,000	666	1,132	1,326	83.4	71.7	66.9
5,000	1,158	1,974	1,530	76.8	60.5	69.4
6,000	2,036	2,223	2,795	66.1	63.0	53.4
7,000	3,904	3,634	4,678	44.2	48.1	33.2
8,000	5,941	7,607	7,008	25.7	4.9	12.4
9,000	8,186	7,301	7,840	9.0	18.9	12.9
10,000	10,326	8,507	9,676	-3.3	14.9	3.2

Table 4: Added and detected total iron concentration and % precipitation in organic-1.5wt%HF acids

Initial iron	**10,000 mg/L (initial)**		**5000 mg/L (initial)**		**1000 mg/L (initial)**	
Acid type	**pH**	**Total iron, mg/L**	**pH**	**Total iron , mg/L**	**pH**	**Total iron, mg/L**
Formic-HF	2.6	9658	2.7	4986	4	1076
	2.8	8155	3.2	650	4.3	
	3.1	4465	4.3	5	4.7	12
	3.3	4321	4.7	0	5.1	0
Acetic-HF	2.7	9889	3.6	4853	4.6	1077
			3.4	2539	4.6	8
	3.4	5397	5	2	5.5	0
	4.2	2660	5.4	8	5.8	0
Citric-HF	2.6	10493	3.4	5117	4.2	1100
	3.1	2719	3.4	975	4.4	12
	4.5	4062	4.6	4	5.1	3
	5.4	5267	5.5	1178	5.7	13

CHAPTER 4

RESULTS AND DISCUSSION (SOLUBILITY TEST)

Sand, kaolinite, illite, and chlorite were reacted with different organic-HF mixtures, prepared using 10 wt% acetic, 9 wt% formic or 10 wt% citric acid and 1.4 or 2.1 wt% ABF. These tests were conducted at 50 and 75°C and atmospheric pressure for 1, 2 and 4 hours. **Table 8** summarizes the main results of these experiments. It was interesting to note that the initial pH value of different organic-HF reaction solutions with sand or clays remained nearly constant even after reaction time of 4 hours.

Solubility of Sand

Sand is mainly composed of quartz and its reaction with organic mud acids produces fluosilicic acid (H_2SiF_6). **Figure 28** shows the silicon concentration in the supernatant of different organic-HF systems at 50 and 75°C. At 50°C, the concentration of dissolved silicon increased with reaction time. Additionally, silicon concentrations in mixtures containing 2.1 wt% ABF were higher than those contained in 1.4 wt% ABF mixtures. For example, 10 wt% citric-2.1 wt% ABF extracted nearly 600 mg/L Si after four hours, while 10 wt% citric-1.4 wt% ABF reaction solution with sand contained only 300 mg/L Si. Similarly, the concentration of extracted Si increased with temperature. All tested organic-HF systems were able to extract more Si when they were reacted with sand at higher temperature, 75°C. For example, the solution of 10 wt%

citric-2.1 ABF acid contained nearly 800 mg/L Si when it reacted with sand for four hours at 75°C, while this acid extracted only 400 mg/L Si at 50°C.

Sand exhibited nearly equal dissolution rates in different organic-HF systems at 50 and 75°C. In addition, the profile of silicon concentration with time indicated that the dissolution rate of sand in each organic-HF remained constant and it did not vary with time, **Figure 28**. These dissolution rates are slow, compared to that of regular mud acid, 12wt% HCl-3 wt% HF. Al-Dahlan *et al*. (2001) reported that regular mud acid extracted 1,600 mg/L Si from sand after four hours at 75°C. **Figure 28** shows that different organic mud acids extracted only 50% of Si concentration contained in reaction solution of regular mud acid with sand at same conditions.

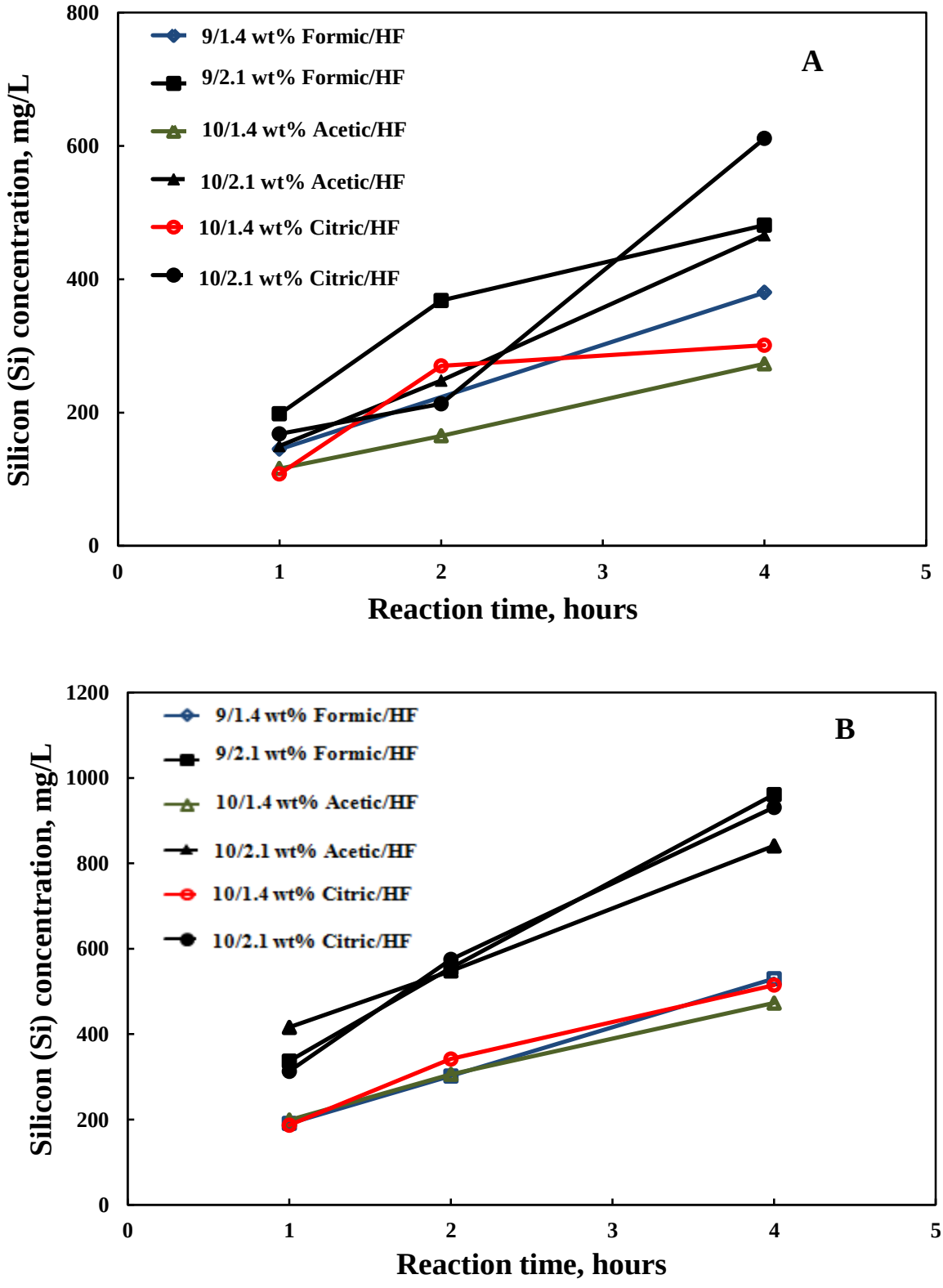

Figure 28: Silicon concentration in reaction solutions of different organic-HF acids and sand at: a) 50°C, and b) 75°C.

Solubility of Kaolinite

Kaolinite is a tetrahedral sheet of Si linked to an alumina octahedral sheet of oxygen, **Figure 6 (Walsh *et al*. 1982, Mitchell 1993)**.Kaolinite contains equal amounts of both aluminum and silicon. Therefore, the Si/Al ratio in supernatants of different organic-HF acids should be unity. The bonding between successive layers is by both van der Waals forces and hydrogen bonds.

Figure 29 shows the Al and Si concentrations in reaction solutions of different organic mud acids with kaolinite, at 75°C, as a function of time. Note the decrease in extracted Si concentration with reaction time. This trend was noticed in all organic mud acids containing 1.4 or 2.1 wt% ABF. However, mixtures of 2.1 wt% ABF had more dissolved silicon ions. For example, reaction solution of 10 wt% formic-2.1 wt% ABF contained nearly 1,000 mg/L Si after four hours, while 10 wt% formic-1.4 wt% ABF had only 500 mg/L Si. In addition, it was interesting to notice that all organic mud acids had comparable dissolved Si content. However, they contained different levels of dissolved Al.

In contrast to Si concentration trend, the Al concentration increased with time in formic and citric mud acids while it almost remained constant in acetic mud acid. The highest Al levels were found in solutions of citric mud acid followed by formic mud mixtures. Compared to these systems, acetic mud acid reaction solutions contained in-significant Al contents. For example, the Al concentrations in 2.1 wt% ABF with 10 wt% citric, 9 wt% formic and 10 wt% acetic acids are 5,500; 4,200; and 500 mg/L, respectively, after reacting with kaolinite for four hours. This low level of Al concentration in acetic mud acid solutions was accompanied with precipitation of Si. Unexpectedly, the Si/Al ratio in spent acetic mud acid solutions was high, ranged between 2 and 4. This indicated that Al might have precipitated in spent acetic mud solutions. This was confirmed by XRF, **Table 5**, and SEM analyses. **Figure 30** shows that Al precipitated as

aluminum fluoride, which agrees with the results of Shuchart and Gdanski (1996).They reported that the reaction of organic mud acid systems, based on acetic and formic, with kaolinite resulted in AlF_3 precipitation. It was interesting to find out that traces of aluminum fluoride was found to be present with kaolinite particles reacted with both formic and citric mud acids. The highest amount of this precipitate was found in spent acetic mud acid followed by formic and citric mud acids. This was mainly attributed to the stronger chelation ability of citric and formic for Al, compared to that of acetic acid. In other words, the precipitation of aluminum fluoride was governed by the bonding strength between Al and organic chelating agent. The presence of organic acids such as citric acid minimized the AlF_3 precipitation.

Again, these systems showed retarded nature when their reaction rate with kaolinite was compared to that of regular mud acid. For example, regular mud acid was able to extract nearly 12,000 mg/L Al from kaolinite after reaction time of 1 hour at 75°C **(Al-Dahlan *et al*. 2001)**. Citric/ABF at 10/2.1 wt% and 9 wt% formic-2.1 wt% ABF were able to extract 40% and 30%, respectively, of the Al levels observed in regular mud acid solutions, **Figure 30**.

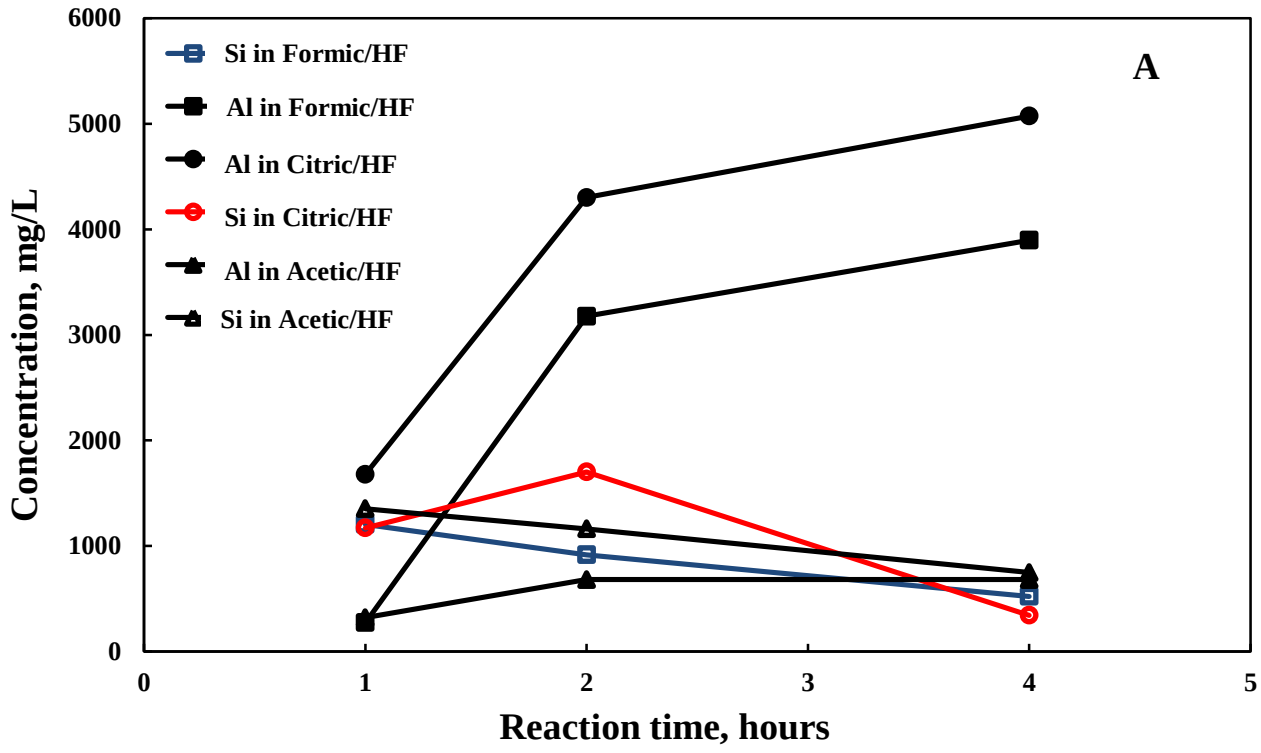

Figure 29: Silicon and aluminum concentrations in reaction solutions of different organic-HF acids and kaolinite at 75°C: a) 1.4 wt% ABF mixtures, and b) 2.1 wt% ABF mixtures.

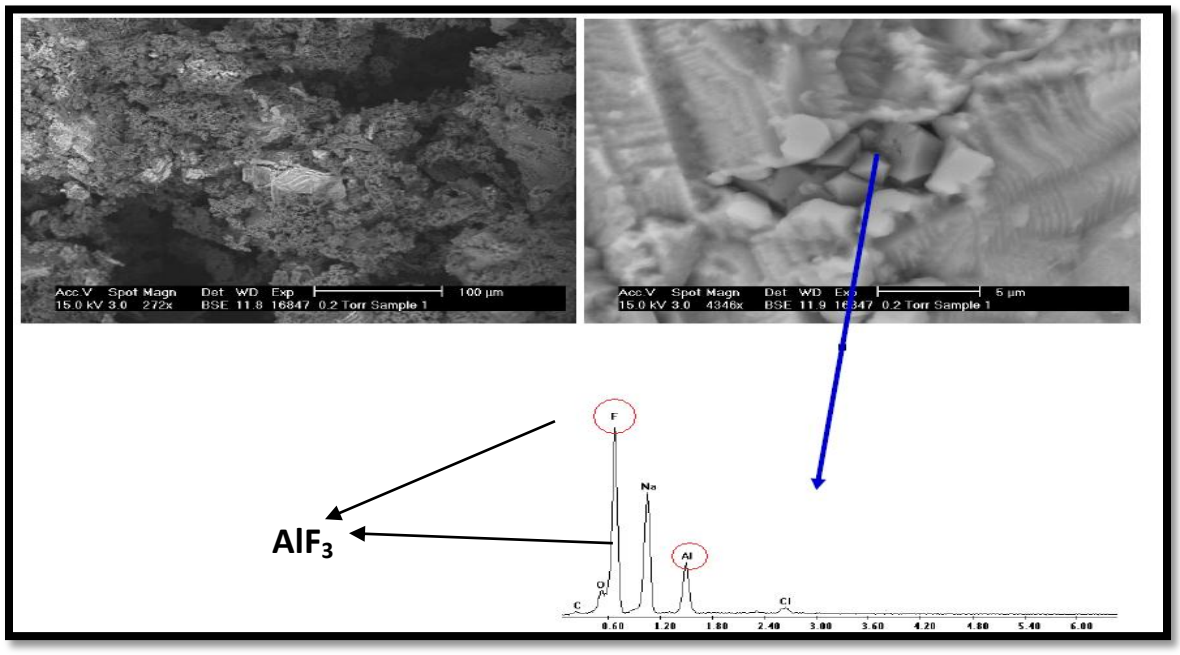

Figure 30: SEM analysis of reacted kaolinite particles with 10 wt% acetic-1.4 wt% ABF at 75°C.

Solubility of Illite

Illite is composed of an aluminum sheet, which is sandwiched by two silica layers. Some randomness in the stacking of layers in illite might occur. Unlike kaolinite, illite has a Si/Al ratio of 2. Consequently, Si concentration is expected to be higher than that of Al and the Si/Al ratio in spent organic mud acid solutions should be nearly 2. Illite might contain potassium ions, where well-organized illite contains 9-10% K_2O **(Walsh *et al*. 1982, Mitchell 1993)**.

Figure 31 shows the aluminum and silicon concentrations in the supernatants of organic-HF systems at 50°C as a function of time. All organic mud acids extracted more silicon than aluminum ions, even when higher amounts of ABF were used, 2.1 wt%. Generally, all organic mud acids had comparable Si levels and similar trend, where the silicon concentration increased with reaction time. For example, 1.4 wt% ABF organic mud acids extracted nearly 800 mg/L Si at 2 hours at 50°C, and gradually extracted more Si ions to reach nearly 1,200 mg/L within 4 hours. Increasing ABF to 2.1 wt% in organic mud acid mixtures resulted in more extracted Si levels. The Si profile in these systems showed similar trend to that of 1.4 wt% ABF orgasmic mud acids, where the Si concentration increased with reaction time. For example, 10 wt% citric-2.1 wt% ABF extracted nearly 1,300 and 1,600 mg/L Si after two and four hours, respectively, at 50°C. Regarding Al extracting power, all organic mud acids showed in-significant levels, when compared to that of Si ions. All systems had nearly equal dissolved Al contents, which slightly increased with reaction time to reach 200 mg/L within four hours. Similarly 2.1 wt% organic mud systems had comparable extracted Al levels, but they contained nearly double the amount of those notice in 1.4 wt% ABF-organic mud systems.

Figure 32 shows the aluminum and silicon concentrations in the supernatants of organic-HF systems at 75°C as a function of time. The increase in reaction temperature resulted in more

extracted Si levels in all organic mud acids. However, the retarded nature of all systems was minimized at 75°C. Around 80% and 75% of the total silicon concentration were dissolved in the first hour in formic-HF and acetic-HF, respectively. In subsequent three hours, the Si concentrations slightly increased with time in all systems except for citric mud mixtures, which showed slight decrease in Si levels. Similarly, significant increase in Al levels was noticed in all organic mud acids when reaction temperature was increased to 75°C. Both acetic and formic mud acids had comparable Al levels, while citric-HF solutions showed higher levels of dissolved Al ions. For example, 10 wt% citric-1.4 wt% contained nearly 800 mg/L after four hours, compared to only 400 mg/L in acetic and formic-1.4 wt% ABF. These levels of Al increased further when ABF was increased from 1.4 wt% to 2.1 wt%.

The relatively low Al concentrations in all organic mud acids was first expected to be due to AlF_3, as noticed in kaolinite solubility tests. However, XRF analysis indicated that there was only 1.78% and 1.5% of fluoride in illite samples when it was reacted with formic-HF and acetic-HF, respectively. Illite reacted with citric-HF had the minimum fluoride weight percentage (1.2%). Based on the percentage of fluoride precipitation, the systems can be arranged in descending order, in terms of AlF_3 precipitation: citric-HF, formic-HF and acetic-HF. This is mainly attributed to the different in chelating ability of these systems for Al, as stated previously.

Based on what described above, it seems that all organic mud acids are not able to extract significant Al ions from illite, when compared to kaolinite. After ruling out the hypothesis based on aluminum fluoride precipitation, the only possible explanation for this trend is the illite structure. Compared to kaolinite, organic mud acids had lower contact surface area with

aluminum sheet, which was protected by two silica layers. As a result, more Si ions were extracted than Al ions, and hence minimal AlF_3 precipitation occurred.

Compared to regular mud acid, these systems were able to dissolve higher Si concentrations and lower Al contents. According to Al-Dhalan (2001), mud acid extracted approximately 6,000 mg/L Al, after three hours, when reacted with illite at 75°C. This amount is considerably greater than the amount detected in organic-HF systems. In contrary, the Si concentration was higher in organic-HF acid solutions and generally did not show the sharp decrease in the Si concentration, which was observed in spent mud acid solutions.

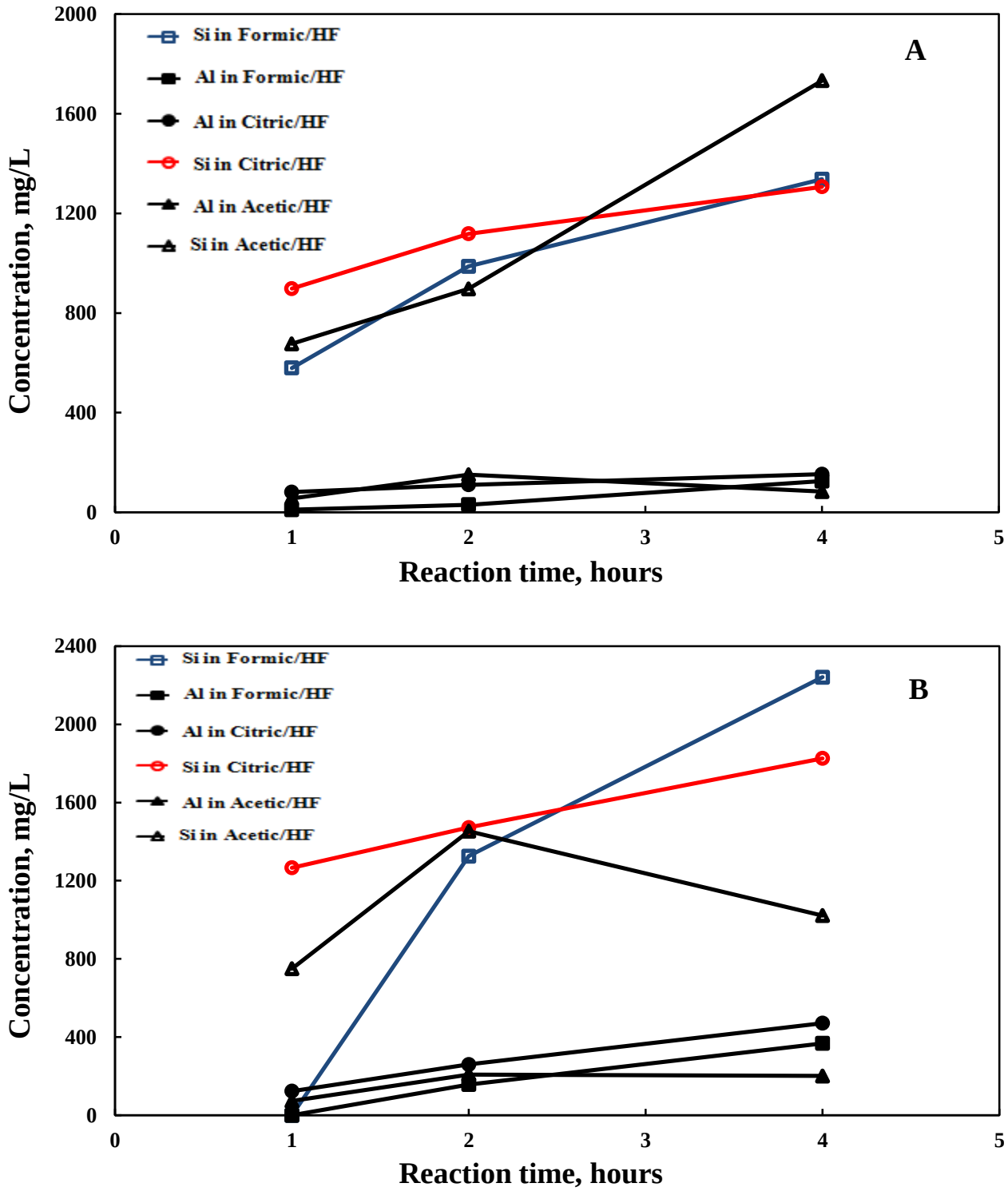

Figure 31: Silicon and aluminum concentrations in reaction solutions of different organic-HF acids and illite at 50°C: a) 1.4 wt% ABF mixtures, and b) 2.1 wt% ABF mixtures.

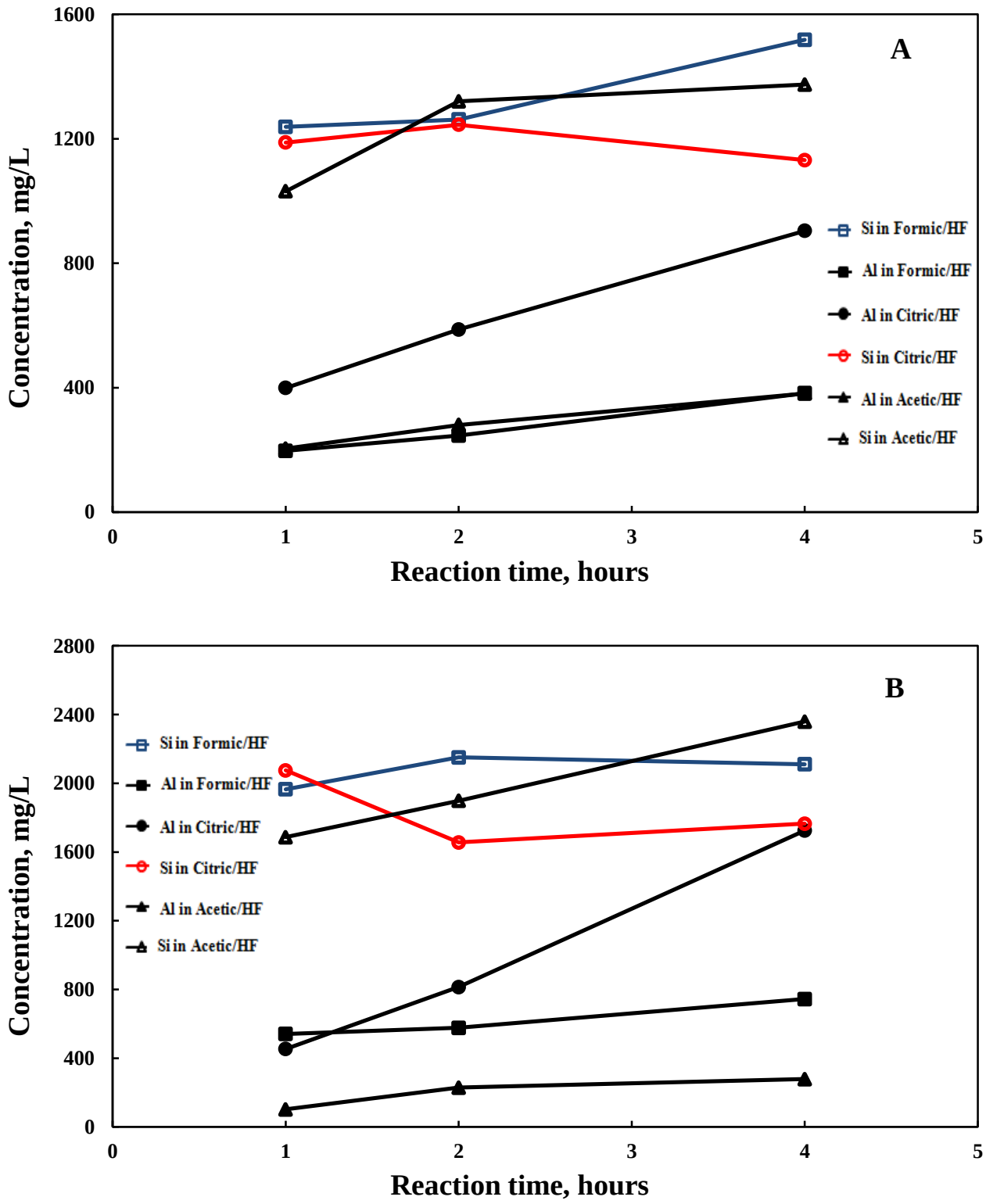

Figure 32: Silicon and aluminum concentrations in reaction solutions of different organic-HF acids and illite at 75°C: a) 1.4 wt% ABF mixtures, and b) 2.1 wt% ABF mixtures.

Solubility of Chlorite

Chlorites are 2:1:1 phyllosilicates minerals. They have a structure that have layer of octahedrally-coordinated Si, Al and Fe in the interlayer space. The 2:1 layers are formed by the stacking of two sheets of tetrahedrally-coordinated silica, and one sheet of octahedraly coordinated Fe or Al between the two tetrahedral sheets **(Walsh *et al*. 1982, Mitchell 1993)**. XRF analysis showed that the chlorite mineral used in this study contained Si, Al, Fe and K ions, **Table 3**.

Figure 33 shows the aluminum and silicon concentrations in the supernatants of organic-HF systems after reaction with chlorite at 50°C, as a function of time. From this figure, it is clear that formic-HF and acetic-HF dissolved roughly the same amount of Si with a little improvement when ammonium bifluoride increased from 1.4% to 2.1%. For example, 9 wt% formic-1.4 wt% ABF extracted nearly 864 mg/L Si within 4 hours and about 1,188 mg/L of silicon was dissolved in 2.1 wt% ABF formic mixture. In comparison, citric mud mixtures dissolved higher amounts of Si ions. Citric-ABF mixtures at 10/1.4 and 10/2.1 wt% dissolved nearly 1,200 and 1,800, respectively, after reaction with chlorite for four hours at 50°C. Almost 90% of extracted Si levels in citric mud acids were reached after reaction time of one hour. In contrast to Si, aluminum levels were not significant in all organic mud acids. XRF analysis showed that 3.2% of the chlorite sample, reacted with formic-HF, was fluoride-based. In acetic-HF and citric-HF, the F-based solids percentages were approximately 2 and 2.5, respectively. The relatively high percentage of fluoride precipitations and low Al concentrations in spent organic mud acid solutions are an indication of aluminum fluoride precipitation. One explanation of this relatively significant AlF_3, compared to illite, is the presence of iron ions. As described previously, all organic acids have higher chelating ability for iron more than that for Al, **Table 1**. As a result,

these acids combined with iron and relatively left high amount of free Al ions to combine with free fluoride ions and precipitate as AlF_3.

At 75°C, all systems were deficient in Al and thus there was no improvement observed in the Al chelating power. The Si concentration increased without any evidence of Si precipitation in acetic-HF, formic-HF and citric-HF. All these systems had comparable Si levels. The retardation nature of these systems decreased with temperature increase. For example, 1.4 wt% ABF-citric mud acids extracted their maximum potential of Si of 1,032 mg/L after 2 hours before it subsequently remained nearly constant with reaction time.

Table 9 shows Fe concentration in different organic mud acids after reacting with chlorite for 4 hours. At 50°C, formic with 1.4 and 2.1 wt% ABF extracted approximately 798 and 1,049 mg/L Fe. Citric-HF and chlorite reaction solutions had comparable Fe levels observed in formic mud acid solutions. Acetic-HF, on the other hand, extracted iron levels almost equal to half what was extracted by the other systems. In contract to formic mud acid, there was no increase in Fe levels extracted from chlorite when the ABF percentage was increased from 1.4 to 2.1. When the temperature increased to 75°C, the amount of iron extracted in each individual system was nearly doubled.

Table 10 shows Fe, Si and Al concentrations in organic acids containing 0.7wt%ABF after reacting with chlorite for 1 hr at 75^{o}C. Formic-0.7wt%ABF could prevent aluminum precipitation partially while complete precipitation of aluminum was noticed in acetic-0.7wt%ABF. On the other hand, citric-0.7wt%ABF was able to prevent aluminum precipitation completely indicated by the Si/Al ratio of 2 which is equivalent to the Si/Al ratio found in the structure of chlorite.

Compared to regular mud acid, all organic-HF showed a retarded nature in Si extraction where mud acid appeared to extract its maximum potential within few minutes **(Al-Dhalan *et al*. 2001)**. On the other hand, regular mud acid was able to extract nearly 1,200 mg/L of Al when reacted with chlorite for 1 hour at 75°C. This is significantly higher than the Al level detected in organic mud acids. This difference observed in dissolved Al levels is mainly due to the aluminum fluoride precipitations occurred in spent organic-HF solutions.

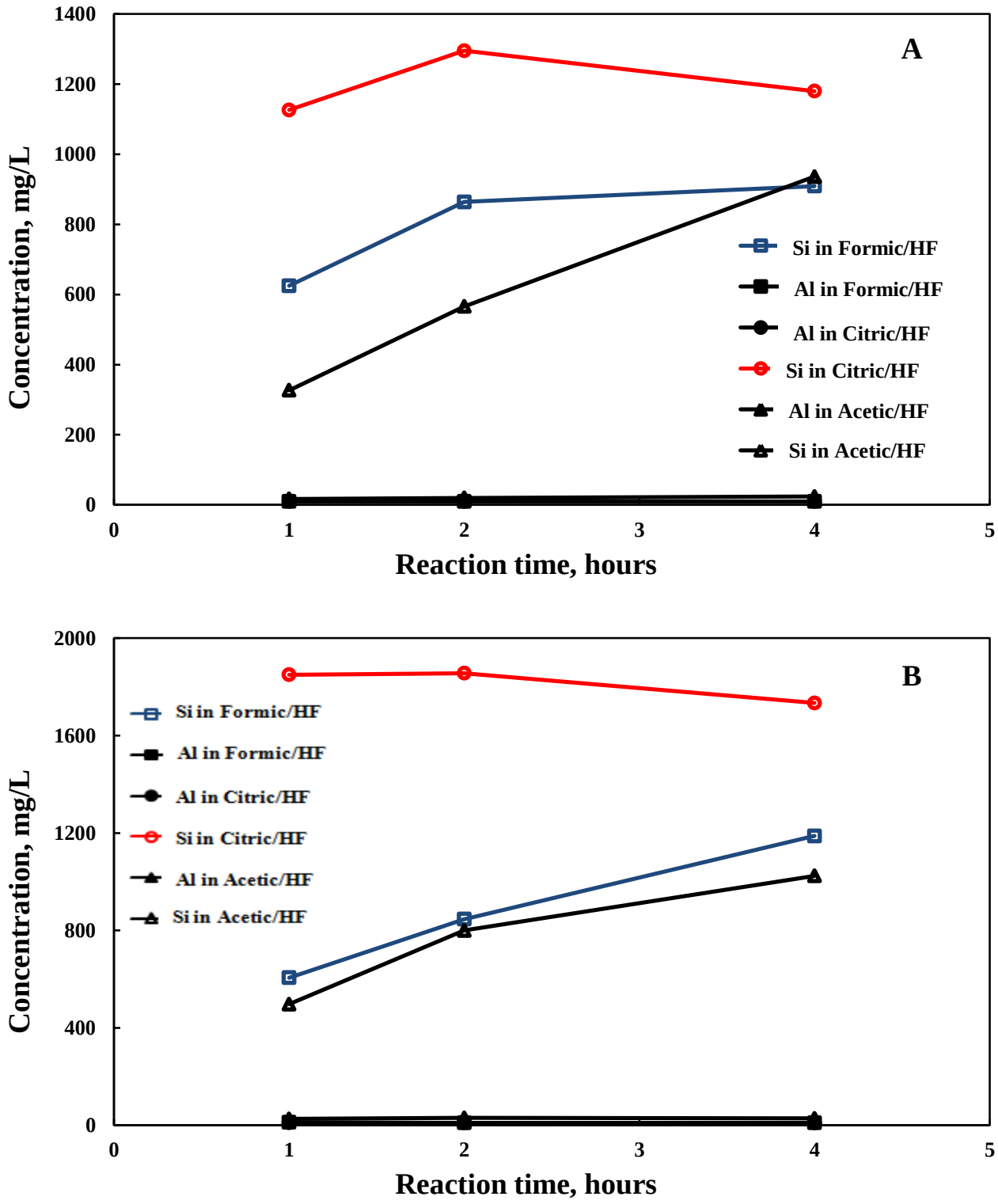

Figure 33: Silicon and aluminum concentrations in reaction solutions of different organic-HF acids and chlorite at 50°C: a) 1.4 wt% ABF mixtures, and b) 2.1 wt% ABF mixtures.

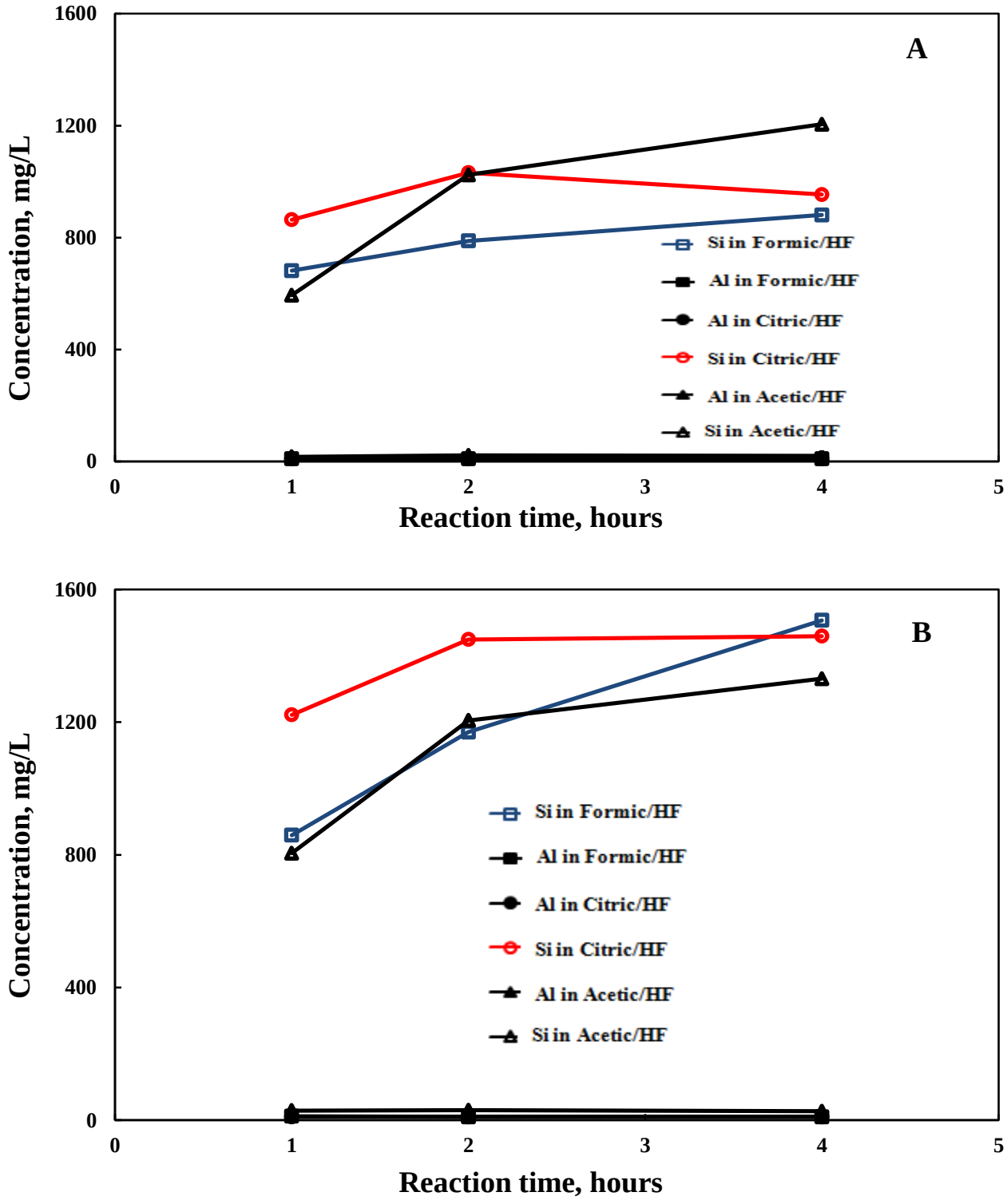

Figure 34: Silicon and aluminum concentrations in reaction solutions of different organic-HF acids and chlorite at 75°C: a) 1.4 wt% ABF mixtures, and b) 2.1 wt% ABF mixtures.

Table 5: Specific surface area of sand, feldspar and clay minerals (Al-Dahlan 2001)

Mineral	**Specific surface are, m^2/g**
Quartz (SiO_2)	2
k-feldspar ($KAlSi_3O_8$)	5-29
Illite/smectite $KAl_4(Si_8,Al)O_{20}(OH)_4/(Ca,Na)(Al,Mg,Fe)_4(Si,Al)_8O_{20}(OH)_4$	82
Kaolinite ($Al_2Si_2O_5(OH)_4$)	15.5
Illite	100-150
Chlorite $(Fe_5Al)(AlSi_3)O_{10}(OH)_8$	20-40
Bentonite	80-700

Table 6: Composition of clay mineral using XRD and XRF analyses

Clay	**XRD**	**XRF, wt%**						
		Al_2O_3	SiO_2	Fe_2O_3	CaO	MgO	Na_2O	K_2O
Kaolinite	> 95 wt%	47.3	51.0	0.30	-	-	-	-
Illite	Quartz and k-feldspar contaminations	25.8	56.6	6.1	0.9	2.5	Trace	7.3
Chlorite	> 99 wt%	20.4	23.4	30.2	0.1	17.1	Trace	Trace

Table 7: Composition of sand using XRF analysis

Element	**Weight percentage (wt%)**
Si	45.7
Al	0.5
Ti	0.05
F	-
K	<0.05
Mg	<0.05
Fe	0.2
O	53.45

Table 8: Summary of experiment and results - Kaolinite

	Organic-ABF system	Time (hr)	pH	Al (mg/L)	Si (mg/L)
Kaolinite at 75°C	9 wt% FORMIC + 1.4 wt% ABF	1	2.76	275	1,205
		2	2.58	3,177	917
		4	2.58	3,896	523
	9 wt% FORMIC + 2.1 wt% ABF	1	2.81	354	1,826
		2	2.84	1,277	1,599
		4	2.86	4,329	923
	10 wt% ACETIC + 1.4 wt% ABF	1	3.75	321	1,353
		2	3.71	683	1,163
		4	3.84	683	749
	10 wt% ACETIC + 2.1 wt% ABF	1	3.81	308	1,796
		2	3.92	478	1,777
		4	3.91	478	1,067
	10 wt% Citric + 1.4 wt% ABF	1	2.82	1,680	1,172
		2	2.7	4,301	1,702
		4	2.8	5,072	344
	10 wt% Citric + 2.1 wt% ABF	1	2.9	798	1,780
		2	2.85	4,690	1,349
		4	2.94	5,575	712

Table 9: Summary of experiment and results - Chlorite

	Organic-ABF system	Time (hr)	pH	Fe (mg/L)	Al (mg/L)	Si (mg/L)
Chlorite at 50°C	9 wt% FORMIC + 1.4 wt% ABF	1	2.41	…	10	625
		2	2.43	…	10	864
		4	2.45	798	10	909
	9 wt% FORMIC + 2.1 wt% ABF	1	2.53	…	12	606
		2	2.57	…	10	846
		4	2.63	1049	10	1,188
	10 wt% ACETIC + 1.4 wt% ABF	1	3.17	…	17	327
		2	3.33	…	20	566
		4	3.59	439	24	936
	10 wt% ACETIC + 2.1 wt% ABF	1	3.26	…	26	497
		2	3.42	…	30	800
		4	3.65	473	28	1,024
	10 wt% Citric + 1.4 wt% ABF	1	2.63	…	10	1,126
		2	2.56	…	10	1,295
		4	2.52	886	10	1,180
	10 wt% Citric + 2.1 wt% ABF	1	2.78	…	10	1,850
		2	2.75	…	10	1,856
		4	2.7	1079	10	1,734
Chlorite at 75°C	9 wt% FORMIC + 1.4 wt% ABF	1	2.5	…	10	682
		2	2.5	…	10	788
		4	2.5	1536	10	881
	9 wt% FORMIC + 2.1 wt% ABF	1	2.64	…	12	859
		2	2.72	…	10	1,170
		4	2.7	1902	10	1,507
	10 wt% ACETIC + 1.4 wt% ABF	1	3.39	…	17	594
		2	3.66	…	22	1,024
		4	3.71	716	20	1,205
	10 wt% ACETIC + 2.1 wt% ABF	1	3.47	…	29	805
		2	3.7	…	30	1,205
		4	3.84	770	27	1,331
	10 wt% Citric + 1.4 wt% ABF	1	2.66	…	10	864
		2	2.62	…	10	1,032
		4	2.59	1985	10	954
	10 wt% Citric + 2.1 wt% ABF	1	2.84	…	10	1,222
		2	2.86	…	10	1,449
		4	2.8	2015	10	1,459

Table 10: Organic mud acids reacted with chlorite for 1 hr at 75^{o}C

Acid Type	**Fe, mg/L**	**Si, mg/L**	**Al, mg/L**
9wt%Formic-0.7wt%ABF	565	354	103
10wt%Acetic-0.7wt%ABF	284	244	<10
10wt%Citric-0.7wt%ABF	921	510	268

Table 11: Summary of experiment and results - Illite

	Organic-ABF system	Time (hr)	pH	Al (mg/L)	Si (mg/L)
Illite at 50°C	9 wt% FORMIC + 1.4 wt% ABF	1	2.64	10	579
		2	2.66	30	987
		4	2.66	125	1,337
	9 wt% FORMIC + 2.1 wt% ABF	1	2.8	**	**
		2	2.79	157	1,326
		4	2.89	368	2,241
	10 wt% ACETIC + 1.4 wt% ABF	1	3.44	56	676
		2	3.55	151	897
		4	3.73	83	1,733
	10 wt% ACETIC + 2.1 wt% ABF	1	3.4	73	750
		2	3.62	208	1,453
		4	3.69	201	1,022
	10 wt% Citric + 1.4 wt% ABF	1	2.72	81	898
		2	2.74	110	1,118
		4	2.72	153	1,307
	10 wt% Citric + 2.1 wt% ABF	1	2.84	123	1,266
		2	2.89	260	1,472
		4	2.92	471	1,826
Illite at 75°C	9 wt% FORMIC + 1.4 wt% ABF	1	2.64	197	1,238
		2	2.56	246	1,262
		4	2.62	382	1,518
	9 wt% FORMIC + 2.1 wt% ABF	1	2.84	541	1,965
		2	2.78	577	2,151
		4	2.74	744	2,111
	10 wt% ACETIC + 1.4 wt% ABF	1	3.68	204	1,031
		2	3.81	280	1,320
		4	3.79	381	1,374
	10 wt% ACETIC + 2.1 wt% ABF	1	3.72	102	1,686
		2	3.86	229	1,898
		4	3.98	278	2,359
	10 wt% Citric + 1.4 wt% ABF	1	2.76	399	1,188
		2	2.75	587	1,245
		4	2.73	904	1,131
	10 wt% Citric + 2.1 wt% ABF	1	2.85	454	2,075
		2	2.89	814	1,656
		4	2.92	1,725	1,765

Table 12: Summary of elemental composition of clays reacted with different 2.1 wt% ABF-organic acids using XRF analysis

Clay Type	Acid Type	Fluoride%	Al%	Si%	O%	Fe%	Mg%	K%
Kalonite	Formic-HF	1.2	23.1	24.6	50.9	0.2	-	-
Kalonite	Acetic-HF	0.89	23.7	24.5	50.7	0.2	-	-
Kalonite	Citric-HF	1	22.3	25.1	51.4	0.2	-	-
Chlorite	Formic-HF	3.2	12	12.9	41.8	19.4	10.7	-
Chlorite	Acetic-HF	1.97	12.3	13.3	42.13	19.2	11.1	-
Chlorite	Citric-HF	2.5	11.8	13.1	42	20	10.6	-
Illite	Formic-HF	1.78	13	25.7	46.88	4.84	1.55	6.25
Illite	Acetic-HF	1.5	13	25.5	47.36	4.9	1.5	6.24
Illite	Citric-HF	1.2	12.8	25.6	47.8	4.9	1.5	6.2

CHAPTER 5

RESULTS AND DISCUSSION (COREFLOOD TESTS)

Coreflood experiments were conducted at 250^{o}F using various organic-hydrofluoric acid mixtures including acetic-HF, formic-HF and citric-HF acids. The base permeability of Berea sandstone plugs was measured by injecting 5wt%NH_4Cl at 5cc/min. As shown in **Figure 35,** When 10wt% acetic acid was injected as preflush at 2cc/min, slight decrease in pressure drop was noticed resulting from dissolving carbonaceous material. The same trend was observed when 9wt% formic acid or 10wt% citric acid were used as a preflush, **Figure 36 and 38** respectively. The effluent of these experiments was analyzed using ICP to measure the ion concentrations. All organic acids have comparable performance in dissolving calcium indicated by the high concentrations of calcium in the effluent samples. In contrast, formic acid was not effective in leaching aluminum or silicon from clays present in Berea sandstone, **Figure 37**. Citric acid, on the other hand, extracted constantly around 1200 mg/L and 500 mg/L of aluminum and silicon respectively, **Figure 39**.

To investigate the effect of HF to improve the permeability of Berea sandstone, main flush consisting of organic acid similar to the preflush containing 1wt%HF was injected through the plug at 2cc/min. As shown in **Figure 38**, when 10wt%acetic-1wt%HF was injected, the pressure drop fluctuated throughout the injection period. The pressure drop after the acid treatment was almost doubled due to severe precipitation of aluminum fluoride. Based on the results of chelation tests and solubility tests reported in chapter 3 and 4 respectively, acetic-HF had more propensities to precipitate aluminum trifluoride compared to formic-HF and citric-HF. So, it was

expected that acetic-HF will damage the core plug. Injecting 9wt%formic-1wt%HF as a main flush had no apparent effect on permeability, **Figure 39**. It can be inferred from **Figure 37** that formic acid dissolved some calcium and formic-HF dissolved some clays but the dissolution of clay minerals was accompanied with precipitation of aluminum fluoride. Besides, there was a slight drop in calcium and magnesium concentrations which might be a result of calcium and magnesium fluoride precipitation. However, the aluminum fluoride precipitate was less than what formed when acetic-HF was used. As a result, there was no change in pressure drop before and after the treatment. The same trend was observed when 10wt%citric-1wt%HF was used as a main acid, **Figure 38**. The permeability ratio was 1.066 when 10wt%citric-1wt%HF was used as main acid.

To further investigate the effect of HF acid to dissolve aluminosilicate minerals, two coreflood experiments were conducted under the same previous conditions with 10wt%citric acid containing 0.5wt%HF and 1.5wt%HF respectively. After injecting 10wt%citric-1.5wt%HF, there was slight increase in pressure drop, **Figure 41**. This might be attributed to the presence of high amount of free fluoride which is prone to precipitate as aluminum fluoride as shown in the previous two chapters. On the other hand, when 10wt%citric-0.5wt%HF was injected as main acid, approximately 15% increase in permeability was achieved (1.19 permeability ratio), **Figure 40**. This confirms the results obtained from chelating tests where aluminum trifluoride was present only in organic-1wt%HF/1.5wt%HF containing low F/Al ratios while organic-0.5wt% was able to prevent AlF_3 formation.

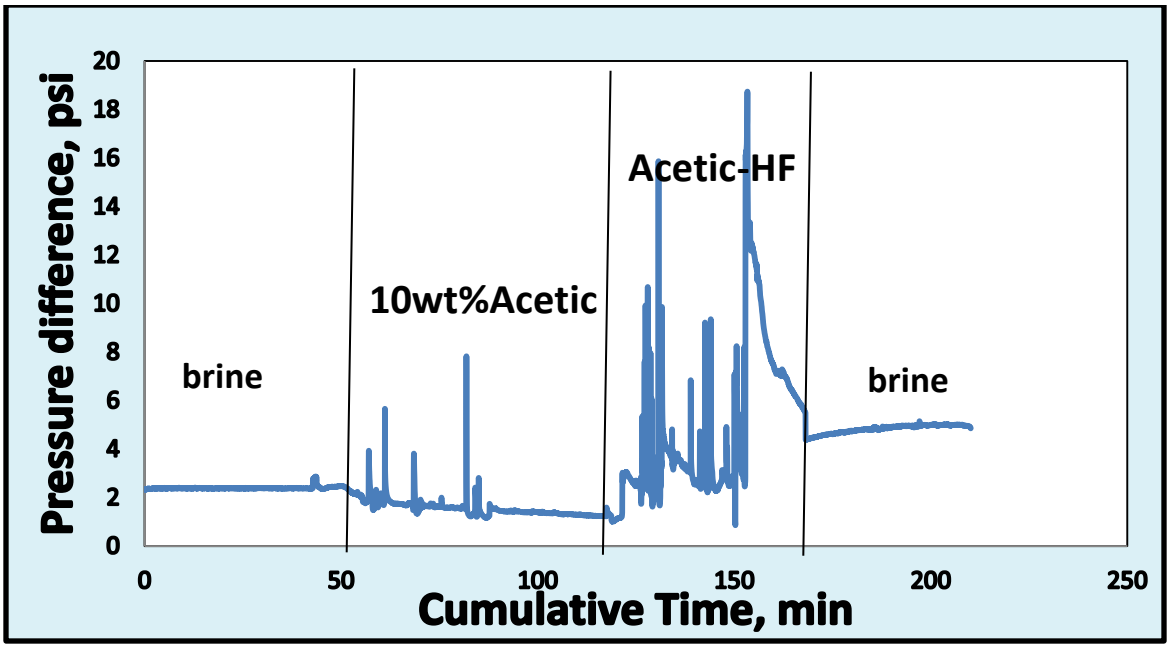

Figure 35: Pressure drop across Berea plug using 10wt% acetic acid as a preflush, 10wt% acetic-1wt%HF as a main flush.

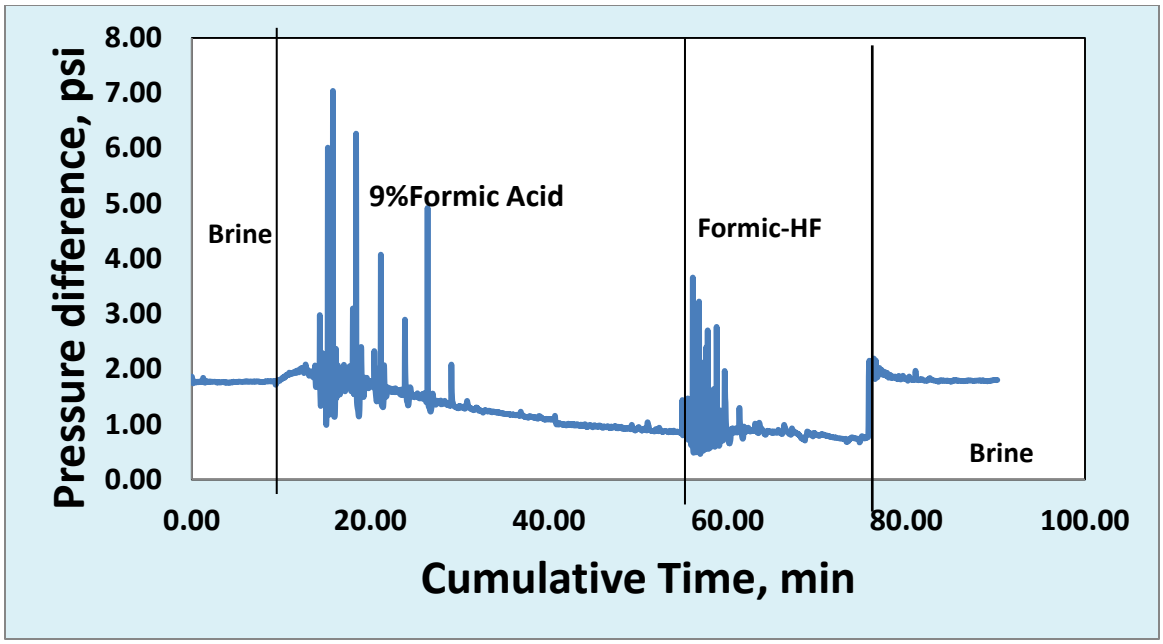

Figure 36: Pressure drop across Berea plug using 9wt% formic acid as a preflush, 9wt% formic-1wt%HF as a main flush.

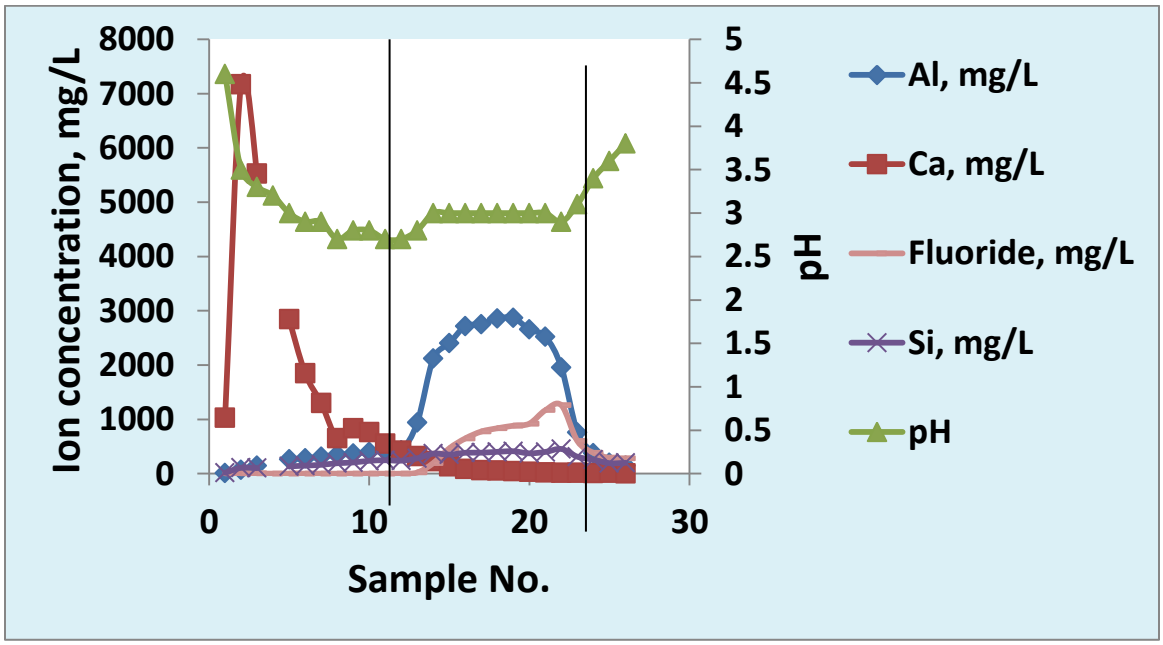

Figure 37: Analysis of coreflood effluent samples for a Berea sandstone treated by 9wt%formic-1wt%HF.

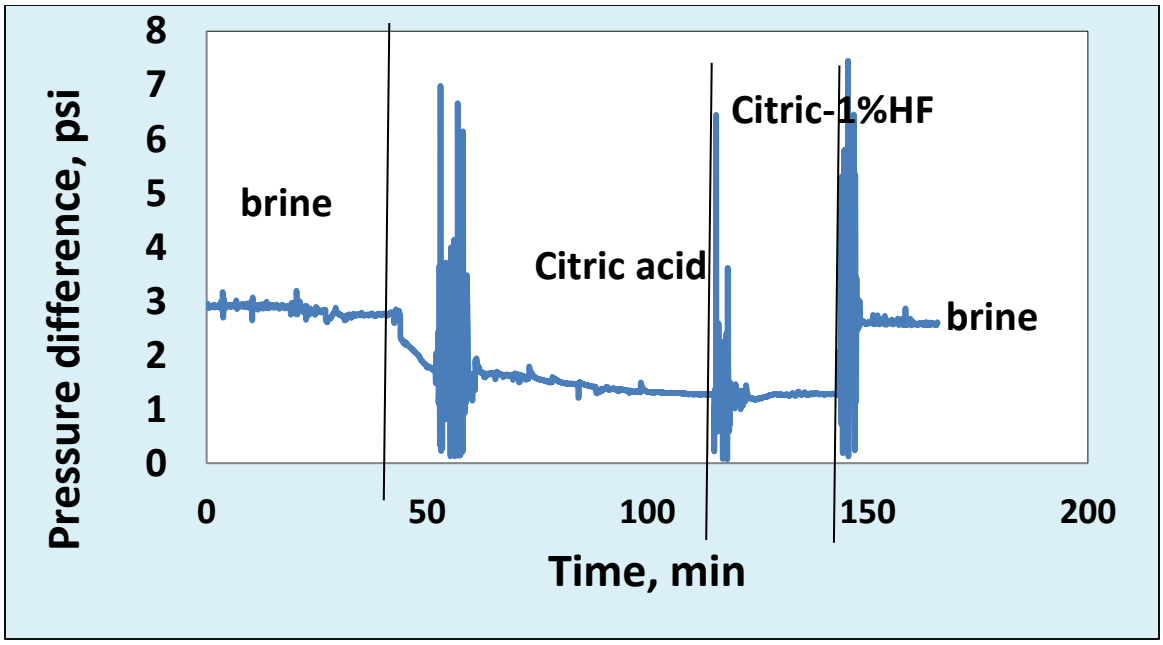

Figure 38: Pressure drop across Berea plug using 10wt%citric acid as a preflush, 10wt%citric-1wt%HF as a main flush

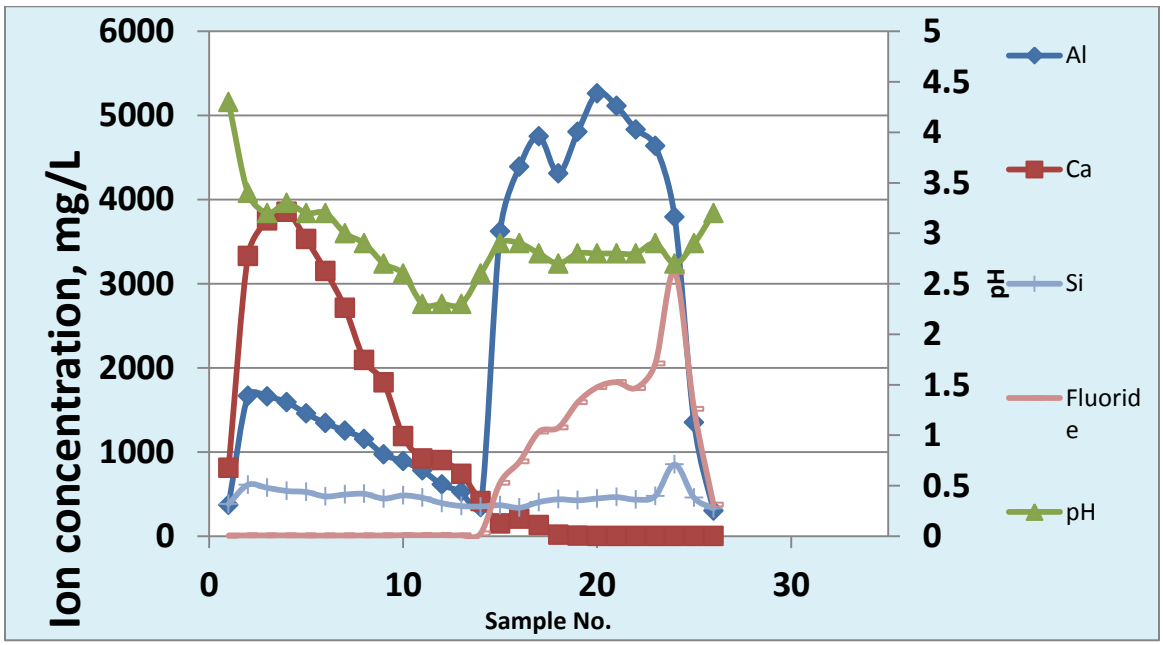

Figure 39: Analysis of coreflood effluent samples for a Berea sandstone treated by 10wt%citric-1.5wt%HF.

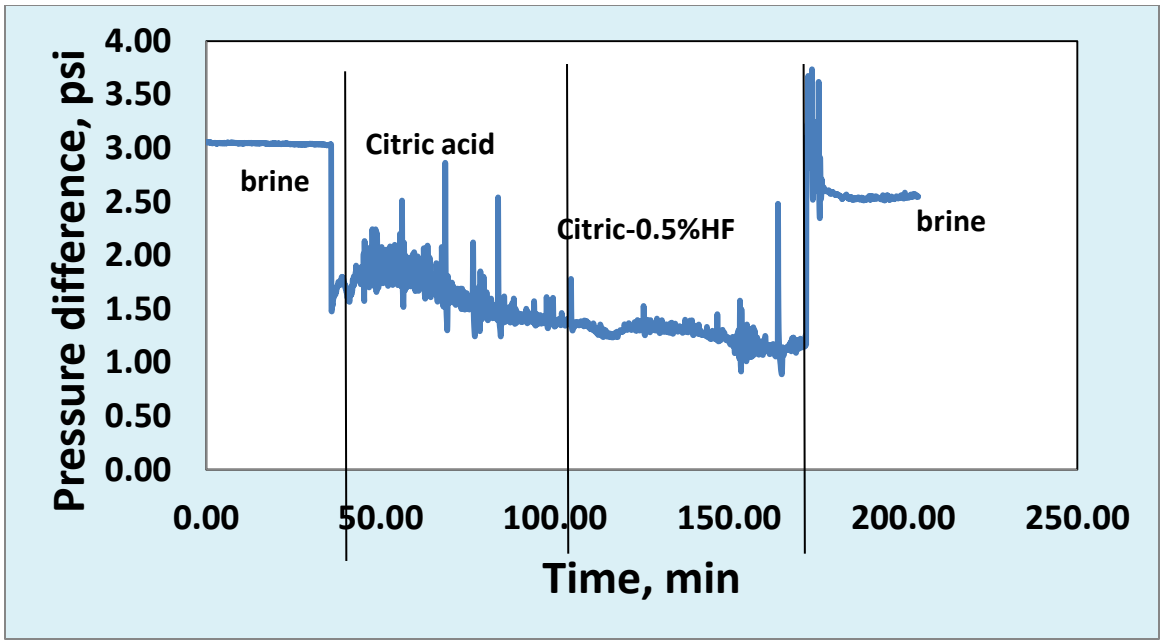

Figure 40: Pressure drop across Berea plug using 10wt%citric acid as a preflush, 10wt%citric-0.5wt%HF as a main flush

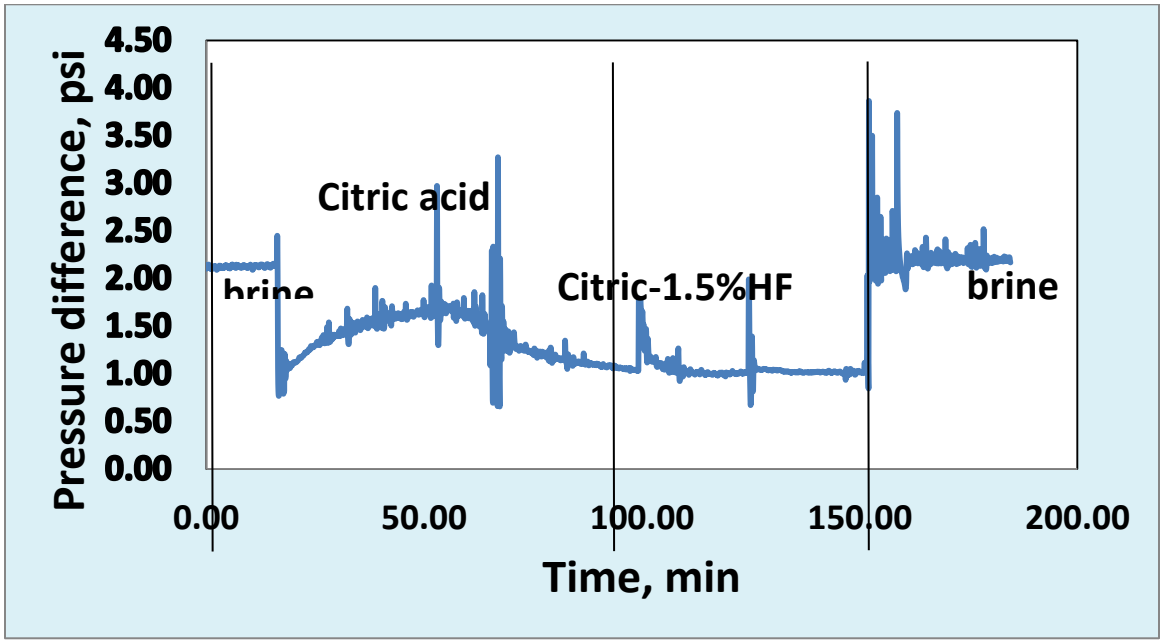

Figure 41: Pressure drop across Berea plug using 10wt%citric acid as a preflush, 10wt%citric-1.5wt%HF as a main flush.

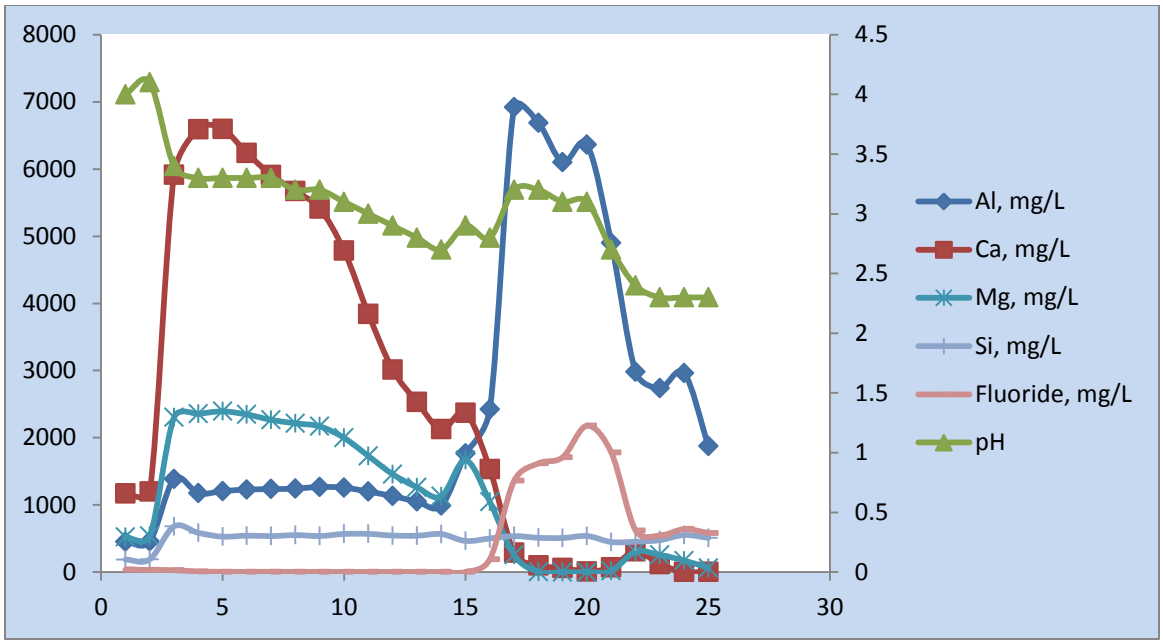

Figure 42: Analysis of coreflood effluent samples for a Berea sandstone treated by 10wt%citric-1.5wt%HF.

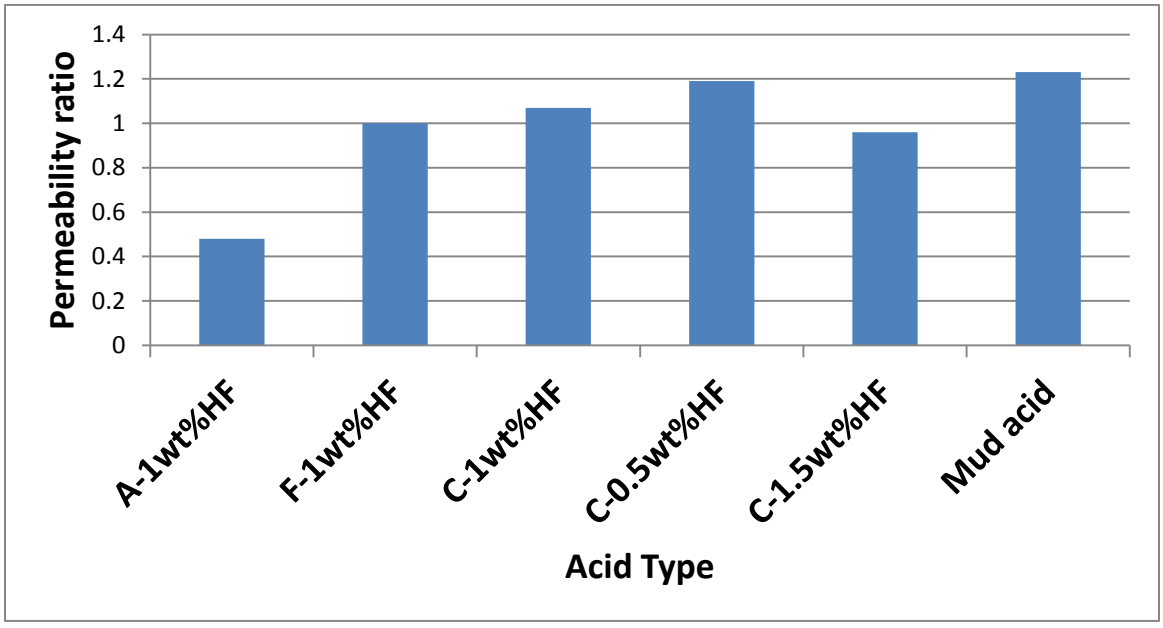

Figure 43: Permeability ratio before and after the acid treatment

CHAPTER 6

CONCLUSIONS

Chelating Tests

- In spite of low initial pH in organic:1.0wt% HF and organic:1.5 wt% HF acids, none of these acids could prevent AlF_3 precipitation. This precipitate was also dependent on F/Al ratio.
- The critical F/Al ratio was found to be approximately 1.9 and whenever F/Al ratio exceeds this value, AlF_3 will form regardless of organic:HF acid type or its solution pH value.
- Formic:HF and acetic:HF precipitated $AlF(OH)_2$ at pH around 5 and above.
- Apparently $AlF(OH)_2$ has less stability than AlF_3 and as a result in citric:HF solutions only AlF3 precipitated while $AlF(OH)_2$ did not form even at higher pH values.

Solubility Tests

The interactions of three different organic mud acids with sand, kaolinite, illite and chlorite were investigated as function of organic/HF ratio, reaction time and temperature values of 50 and 75°C. The three organic-HF systems were prepared using 10 wt% acetic, 9 wt% formic and 10 wt% citric acids, mixed with 1.4 or 2.1 wt% ABF. The main conclusions of this study were:

Acetic-HF acid:

- Compared to regular mud acid, this system showed retarded reaction nature with sand. At the same conditions, this system extracted only 50% of Si concentration contained in reaction solution of regular mud acid with sand.
- Higher amounts of extracted Si during the reaction of this system with sand were observed when both the reaction temperature and ABF wt% were increased.
- During the reaction of this system with kaolinite, silica gel and aluminum fluoride precipitations were noticed. Aluminum fluoride precipitation during the reaction of this system with kaolinite was higher than those occurred in formic and citric mud acids.
- The degree of aluminum precipitation during acetic-ABF reaction with illite was much lower than that observed in kaolinite reaction. This mainly was attributed to illite structure which resulted in the extraction of high Si ions and low Al levels. No indication of silica gel precipitation was noticed during the reaction of this system with illite.
- Highest amount of AlF_3 were noticed in this system when it reacted with chlorite mineral. This mainly was attributed to the presence of iron ions which prevented the chelation of Al ions by acetate ions.

Formic-HF acid:

- This system showed comparable performance with both acetic and citric when it reacted with sand at 50°C and 75°C.
- Higher amounts of extracted Si during the reaction of this system with sand were observed when both the reaction temperature and ABF wt% were increased.
- During the reaction of this system with kaolinite, silica gel and aluminum fluoride precipitations were noticed. Although this system showed same degree of silica gel precipitation, noticed during acetic mud acid reactions, aluminum fluoride precipitation during the reaction of this system with kaolinite was much lower than those occurred in acetic acid-HF reaction with kaolinite.
- Compared to regular mud acid, this system showed retarded reaction rate with illite. There was no indication of silica gel precipitation and aluminum fluoride precipitation was minimal.
- Highest amount of AlF_3 was noticed in this system when it reacted with chlorite mineral. This mainly was attributed to the presence of iron ions which prevented the chelation of Al ions by formate ions. Compared to acetic mud acid, the amount of this precipitate was low.

Citric-HF acid:

- When it was reacted with sand, this system extracted comparable levels of Si ions to those present in spent solutions of formic and acetic mud acids.
- During the reaction of this system with kaolinite, same degree of silica gel precipitation, occurred in acetic and formic mud acids, was noticed. AlF_3 precipitation was much lower than those observed in other organic mud acids reaction solutions.
- Compared to regular mud acid, this system showed retarded reaction rate with illite. There was no indication of silica gel precipitation and aluminum fluoride precipitation was minimal.
- Due to the high chelation ability of citrate ion for Al, citric-HF extracted more Al than what other systems did when reacted with kaolinite and illite. However, AlF_3 precipitation was relatively significant when this system reacted with chlorite. This is mainly due to the presence of competing iron ions.

Based on the above conclusions, it is clear that acetic-HF, formic-HF and citric-HF are suitable for stimulating clean sandstone formations. Only formic-HF and citric-HF can be used to stimulate sandstone formations mixed with illite and/or kaolinite. However, these organic mud acid systems except citric-0.5wt%HF should not be used for formations containing chlorite clays due to severe aluminum fluoride precipitation.

Coreflood Tests

- Acetic, formic and citric acids had comparable performance in dissolving calcium from sandstone plugs.
- While preflush of citric acid could extract aluminum and silicon from the plugs, both acetic and formic were not effective in leaching Al and Si.
- When 10wt%acetic-1wt%HF was used as a main flush, the pressure drop was almost doubled due to severe precipitation of aluminum trifluoride.
- Compared to 10wt%acetic-1wt%HF, 9wt%formic-1wt%HF and 10wt%citric-1wt%HF dissolved more aluminum and didn't cause apparent damage.
- The optimum HF concentration was found to be 0.5wt% resulted in 19% increase in permeability.

References

1.Abrams, A., Scheuerman, R.F., Templeton, C.C and Richardson, E.A., 1983. Higher-pH Acid Stimulation Systems. *J. Pet. Tech*., December, 2175-84.

2. Al-Mohammad, A.M., Nasr-El-Din, H.A., Al-Aamri, A.M. and Al-Fuwaires, O. 2006. Reaction of Calcite with Surfactant-Based Acids. Paper SPE 102838 presented at the SPE Annual Technical Conference and Exhibition, San Antonio, TX September 24-27.

3.Al-Dahlan, M.N., Nasr-El-Din, H.A., and Al-Qahtani, A.A., 2001. Evaluation of Retarded HF Acid Systems. Paper SPE 65032, presented at the SPE International Symposium on Oil Field Chemistry, Houston, Texas, 13-16 February.

4.Al-Khaldi, M.H., Nasr-El-Din, H.A., Blauch, M.E., and Funkhouser, G.P., 2005. New Findings on Damage Potential, Geochemical Reaction Mechanisms, and Production Enhancement Applications for Citric Acid. *SPEJ*, 10(**3**), 267-275.

5.Baofeng, W, Weidong, J., Xihua, L. and Puyong, F., "Acidizing High-Pressure Water Injection Wells Using a New Low Damage Acetic/HF Acid System" paper SPE 64776 presented at the SPE International Oil and Gas Conference and Exhibition, Beijing, China, Nov. 7-10, 2000.

6.Blake, R.E. and Walter, L.M., 1999. Kinetics of Feldspar and Quartz Dissolution at 70-80 and Near-Neutral pH: Effects of Organic Acids and NaCl. Geochim. Cosmochim. Acta, 63, 2043-59.

7. Brady, J.L., Gantt, L.L., Fife, D.M., Rich, D.A and Almond, S.W., 1989. Cement Solubility in Acids. Paper SPE 18986 presented at the SPE Joint Rocky Mountain Regional/Low Permeability Reservoirs Symposium and Exhibition, Denver, Mar. 6-8.

8. Boggs, Sam. 2006. Principles of Sedimentology and Stratigraphy.

9. Chang, F.F., Nasr-El-Din, H.A., Lindvig, T and Qiu, X.W., 2008. Matrix Acidizing of Carbonate Reservoirs Using Organic Acids and Mixture of HCl and Organic Acids. Paper SPE 116601 presented at SPE Annual Technical Conference and Exhibition, Denever, Colorado, September 21-24.

10. Crowe, C.W., 1985. Evaluation of Agents for Preventing Precipitation of Ferric Hydroxide from Spent Treating Acid. JPT, 691-695.

11. Crowe, C.W., 1986. Precipitation of Hydrated Silica from Spent Hydrofluoric Acid – How Much of a Problem is it?.*JPT,* 1234 - 1244.

12. David, A., Qi Qu and Richard, K. 2003. The Development and Successful Field Use of Viscoelastic Surfactant-Based Diverting Agents for Acid Stimulation. Paper SPE 80222 presented at the SPE International Symposium on Oilfield Chemistry, Houston, Texas, Feb. 5-7.

13. Franco, C.A., Solares, J.R., Al-Marri, H.M., Mukhles, A.E., Ramadhan, N.H. and Saihati, A.H., 2010. Analysis of Deposition Mechanism of Mineral Scales Precipitating in the Sandface and Production Strings of Gas-Condensate Wells. SPE P&O, May, 161-171.

14. Gatewood, J.R., Hall, B.E., Roberts, L.D. and Lasater, R.M., 1970. Predicting Results of Sandstone Acidizing. JPT, 693-700.

15. Gdanski, R.D., 1985. $AlCl_3$ Retards HF Acid for More Effective Stimulation. *OGJ,* October, 111-115.

16. Gdanski, R.D., 1996. Kinetics of the Tertiary Reaction of HF on Alumino-Silicate. Paper SPE 31076, presented at the SPE Formation Damage Symposium, Lafayette, Feb. 14-15.

17. Gdanski, R.D. and Shuchart, C.E., 1996. Newly Discovered Equilibrium Controls HF Stoichiometry. *JPT*, 48(**2**), 145-149.
18. Gdanski, R.D. and Shuchart, C.E., 1997. HF Acid Blends Based on Formation Conditions Eliminate Precipitations Problems. Hart's Petroleum Engineer International, March, 63-66.
19. Gidley, J.L., 1985. Acidizing Sandstone Formations: A Detailed Examination of Recent Experience. Paper SPE 14164, presented at the SPE Annual Technical Conference and Exhibition, Las Vegas, Nevada, 22-26 September.
20. Hall, B.E. and Dill, W.R., 1988. Iron Control Additives for Limestone and Sandstone Acidizing of Sweet and Sour Wells. Paper SPE 17157, presented at the SPE Formation Damage Control Symposium, Bakersfield, 8-9 February.
21. Harris, F.N. 1961. Applications of Acetic Acid to Well Completions, Stimulations and Reconditioning. JPT 13(7) 637-639.
22. Hartman, R.L., Lecerf, B., Frenier, W., Ziauddin, M. and Fogler, H.S., 2003. Acid Sensitive Aluminosilicates: Dissolution Kinetics and Fluid Selection for Matrix Stimulation Treatments. Paper SPE 82267, presented at the SPE European Formation Damage Conference, The Hague, Netherlands 13-14 May.
23. Martell, A. E., Smith, R. M., 1976. Critical Stability Constants, Vol. 1–4. Plenum Press: New York, USA.
24. Martell, A.E., Hancock, R.D., Smith, R.M. and Motekaitis, R.J., 1995. Coordination of Al(III) in the environment and in Biological Systems. Coordination Chemistry Reviews, 311-28.
25. McLeod, H.O.:"Matrix Acidizing" JPT (Dec. 1984) 2055-69

26. Mitchell, J.K., 1993. Fundamentals of Soil Behavior 2nd edition. John Wiley & Sons, (Chapter 3).
27. Motta, E.P., Miranda, C.R., Anjos, S.M.C. and Ribeiro, J.A., 1996. Acidizing Wells With Acetic/HF Mixtures to Minimize Cement Dissolution. Paper SPE 31080, presented at the SPE International Symposium, Lafayette, 14-15 February, 1996.
28. Navarrete, R.C., Holms, B.A., McConnell, S.B. and Linton, D.E. 1998. Emulsified Acid Enhances Well Production in High Temperature Carbonate Formations. Paper SPE 50612, presented at the SPE European Petroleum Conference, the Hague, the Netherlands, Oct. 20-22.
29. Perrin, D., 1981. Dissociation Constants of Organic Bases in Aqueous Solution. Butterworths, London, UK.
30. Rae, P and Lullo, G.: "Matrix Acid Stimulation-A Review of the State of the Art" paper SPE 82260 presented at the SPE European Formation Damage Conference, the Hague, the Netherlands 13-14 May 2003.
31. Rietjens, M., 1998. Decomplexation of Aluminum-Fluoride Complexes by Citrate Based Buffers as a Function of pH, Aluminum and Fluoride Concentrations. ACTA, February, 265-73.
32. Robert, J.A. and Crowe, C.W., 2000. Carbonate Acidizing Design," Reservoir Stimulation. John Wiley and Sons Inc., New York City, 17-11.
33. Rogers, B. A., Burk, M.K. and Stonecipher, S.A., "Designing a Remedial Acid Treatment for Gulf of Mexico DeepwaterTurbidite Sands Containing Zeolite Cement" paper SPE 39595 presented at the SPE International Symposium on Formation Damage Control, Lafayette, Louisiana, Feb. 18-19, 1998.

34. Serjeant, E. P., and Dempsey, B., 1979. Ionization Constants of Organic Acids in Aqueous Solution. Pergamon Press: Oxford, USA.

35. Shaughnessy, C.M. and Kunze, K.R., 1981. Understanding Sandstone Acidizing Leads to Improved Field Practices. *JPT* (July), 1196-1202

36. Shuchart, C.E., 1995. HF Acidizing Returns Analyses Provide Understanding of HF Reactions. Paper SPE 30099, presented at the SPE European Formation Damage Symposium, the Hague, Netherlands, May 15-16.

37. Shuchart, C.E., 1997. Chemical Study of Organic-HF Blends Leads to Improved Fluids. Paper SPE 37281, presented at the SPE International Symposium, Houston, 18-21 February.

38. Shuchart, C.E. and Gdanski, R.D., 1996. Improved Success in Acid Stimulations with a New Organic-HF System. Paper SPE 36907, presented at the European Petroleum Conference, 22-24 October.

39. Simon, D.E. and Anderson, M.S., 1990. Stability of Clay Minerals in Acid. Paper SPE 19422, presented at the Formation Damage Control Symposium, Lafayette, February 22-23.

40. Smith, C.F. and Hendrickson, A.R., 1965. Hydrofluoric Acid Stimulation of Sandstone Reservoirs. *JPT*, 17(**2**), 215-222.

41. Stoessell, R.K. and Pittman, E.D., 1990. Secondary Porosity Revisited: the Chemistry of Feldspar Dissolution by Carboxylic Acids and Anions. The American Association of Petroleum Geologists, 74(**12**), 1795-1805.

42. Taq, A.A., Nasr-El-Din, H.A. and Shafei, T.A., 2009. A New Technique to Enhance Cement Resistance to Mud Acids. Paper SPE 119994, presented at the SPE European Formation Damage Conference, 27-29 May.

43. Taylor, K.C., Nasr-El-Din H.A. and Al-Alawi, M., 1999. Systematic Study of Iron Control Chemicals Used During Well Stimulation SPEJ 4, 19-24

44. Thomas, R.L., Nasr-El-Din, H.A., Lynn, J.D., Mehta, S. and Zaidi, S.R., 2001. Precipitation During the Acidizing of a HT/HP Illitic Sandstone Reservoir in Eastern Saudi Arabia: A Laboratory Study. Paper SPE 71690, presented at the SPE Annual Technical Conference and Exhibition, New Orleans, Louisiana, 30 September-3 October.

45. Thomas, R.L., Nasr-El-Din, H.A., Mehta, S., Hilab, V. and Lynn, J.D., 2002. The Impact of HCl to HF Ratio on Hydrated Silica Formation During the Acidizing of a High Temperature Sandstone Gas Reservoir in Saudi Arabia. Paper SPE 77370, presented at the SPE Annual Technical Conference and Exhibition, San Antonia, TX, 29 September-2 October.

46. Walter, R.D. and Keeney, B.R. 1978. Optimizing HCl-Formic Acid Mixtures for High Temperature Stimulation. paper SPE 7567 presented at the SPE Annual Technical Conference and Exhibition, Houston, 1-3 Oct..

47. Wehunt, C.D., Howard, V.A., Warner, J.L. and Ali, S.A., 1993. Laboratory Acidization of an Eolian Sandstone at 380^{o}F paper SPE 25211 presented at the SPE International Symposium on Oilfield Chemistry, New Orleans, LA, U.S.A, March 2-5.

48. Williams, B.B., Gidley, J.L., and Schechter, R.S. 1979. Acidizing Fundamentals. Monograph Series, SPE, Dallas.

49. Yokel, R.A., 2002. Aluminum Chelation Principles and Recent Advances. Coordination Chemistry Reviews, 228,97-113.

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